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Washington, D. C. ▼ June 9, 1923

CHEMICAL, PHYSICAL, AND INSECTICIDAL PROPERTIES OF ARSENICALS

By

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Bureau of Entomology

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By F. C. Cook, *Physiological Chemist, Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry,* and N. E. McIndoo, *Insect Physiologist, Fruit Insect Investigations, Bureau of Entomology.*[1]

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PURPOSE OF INVESTIGATION.

A study of the chemical, physical, and insecticidal properties of arsenicals on the market was undertaken in order to gain a better understanding of them, to be able, if possible, to improve them, and to produce new arsenicals for insecticidal purposes. The results of this investigation, which was conducted by the Bureau of Chemistry and the Bureau of Entomology of the United States Department of Agriculture, are here reported.

ARSENICALS STUDIED.

Paris green and lead arsenate, which have been standardized and found reliable for many years, have constituted the principal insecticides used against external chewing insects. However, during the past few years, the use of calcium arsenate has steadily increased, owing in part to the discovery that it is effective in combating the boll weevil. The manufacture of calcium arsenate, although well beyond the experimental stage in most factories, probably will not be completely standardized for several years. Because of the importance and recent large-scale production of calcium arsenate, many of the results in this bulletin deal with comparisons of calcium arsenate and acid lead arsenate.

[1] The following assisted in this work: R. Elmer, W. A. Gersdorff, R. Jinkins, B. Neuhausen, and A. Schultz, Junior Chemists, Insecticide and Fungicide Laboratory, Bureau of Chemistry, and W. A. Hoffman, Scientific Assistant, and W. B. Wood, Entomological Assistant, Bureau of Entomology.

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The arsenicals analyzed in this investigation, many of which were used in the entomological tests (pp. 26–50), were obtained on the market in 1916. The samples were used as purchased, with the exception of the paste products which were dried before being used. Samples of the following arsenicals were studied: Arsenious oxid (4 samples), arsenic oxid (2 samples), acid lead arsenate (18 samples), basic lead arsenate (2 samples), calcium arsenate (9 samples), zinc arsenite (2 samples), Paris green (2 samples), mixture of calcium and lead arsenates (2 samples), sodium arsenate (2 samples), potassium arsenate (1 sample), London purple (1 sample), and magnesium arsenate (1 sample). Several samples of acid and basic lead arsenate and of calcium arsenate, and one of barium arsenate, one of aluminum arsenate, and one of copper barium arsenate mixture were prepared in the laboratory, analyzed, and tested on insects.

Various names are applied to the arsenicals here designated as (*a*) acid lead arsenate, (*b*) basic lead arsenate, (*c*) arsenious oxid, and (*d*) arsenic oxid. Some of these names are incorrect because they are based on erroneous analyses or interpretations of composition, for example, ''neutral lead arsenate'' for a basic lead arsenate. Some are considered not to be in good usage, according to modern chemical writing, for example, ''arsenious acid'' for arsenious oxid. Arsenious oxid dissolved in water forms arsenious acid. The same relation exists between arsenic oxid and arsenic acid. Other names, although correct, are unnecessarily involved, for example, ''hydroxy-lead arsenate'' for basic lead arsenate. The terms selected for use in this bulletin are both scientifically correct and commonly applied to arsenicals. Their names, with the synonyms, are as follows:

(*a*) Acid lead arsenate ($PbHAsO_4$).
- Ordinary lead arsenate.
- Hydrogen lead arsenate.
- Diplumbic arsenate.
- Dilead arsenate.
- Diplumbic hydrogen arsenate.
- Bibasic arsenate.

(*b*) Basic lead arsenate ($Pb_4(PbOH)(AsO_4)_3$. H_2O).
- Triplumbic arsenate (T. P. arsenate).[2]
- Neutral lead arsenate.[2]
- Trilead arsenate.[2]
- Nonacid lead arsenate.
- Hydroxy-lead arsenate.
- Lead ortho arsenate.[2]

(*c*) Arsenious oxid (As_2O_3).
- Arsenic.
- White arsenic.
- Arsenious anhydrid.

(*d*) Arsenic oxid (As_2O_5).
- Arsenic pentoxid.
- Arsenic anhydrid.

CHEMICAL PROPERTIES OF ARSENICALS.

OXIDS OF ARSENIC.

Arsenious oxid (As_2O_3), commonly called white arsenic or simply arsenic, is the basis for the manufacture of all arsenicals. In the United States arsenious oxid is a by-product from the smelting of lead, copper, silver, and gold ores, being recovered from the flue dust and fumes. The arsenious oxid first sublimed is impure, owing to the presence of carbon and sometimes of sand. The impure oxid may then be resublimed to give a relatively pure oxid, consisting of approximately 99 per cent of arsenious oxid and a trace of arsenic oxid (As_2O_5). Between 11,000 and 12,000 tons of arsenious oxid were produced in the United States in 1920, more than half of which was

[2] These names are incorrect, having been used when basic lead arsenate was considered to be trilead arsenic.

used for insecticide purposes. Canada, Mexico, England, Germany, France, Japan, and Portugal produce large quantities of arsenious oxid.

There are three forms of arsenious oxid: (*a*) The amorphous, vitreous, or glassy form; (*b*) the ordinary crystalline ("octahedral") form; and (*c*) the orthorhombic crystalline form. The amorphous form changes spontaneously into the crystalline form on standing. The trade usually recognizes two grades of arsenious oxid, the light and the heavy forms, although they are the same chemically.

The literature contains conflicting statements concerning the solubility of arsenious oxid in water. Because of the slowness with which arsenious oxid goes into solution, many weeks being required to dissolve even a small sample of the solid, it is probable that in all of the reported results equilibrium had not been reached. The varying percentages of crystalline and amorphous material present in the samples tested, the amorphous form being more soluble than the crystalline forms, may possibly help to account for these discrepancies.

With the exception of Paris green, the arsenites are prepared by combining arsenious oxid and the base.

As a rule, arsenates are made by the direct action of arsenic acid in solution on a metallic oxid. The arsenic acid used for this purpose is manufactured from arsenious oxid by oxidation, usually by means of nitric acid, but sometimes by other oxidizing agents.

The analytical results here reported are based on the weights of the original samples. The methods of analyses used were in general those of the Association of Official Agricultural Chemists (*1*).[3]

Table 1 gives the analytical results on the six samples of arsenious and arsenic oxids selected to represent the arsenical materials used in the manufacture of arsenicals.

TABLE 1.—*Composition of arsenious oxid (As_2O_3) and arsenic oxid (As_2O_5) used in manufacturing arsenicals.*

Sample No.	Material analyzed.	Moisture.	Total arsenious oxid (As_2O_3).	Total arsenic oxid (As_2O_5).	Water-soluble arsenious oxid (As_2O_3).[1]	Water-soluble arsenic oxid (As_2O_5).[1]
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
9	Laboratory arsenious oxid	0.20	99.80	.....	17.77	.....
19	Commercial arsenious oxid	.99	99.01	.....	24.56	.....
27	.....do	.71	99.29	.....	38.00	.....
37	.....do	.15	99.22	.....	30.26	.....
10	Laboratory arsenic oxid (solid arsenic acid)	.....	.....	77.27	.....	77.27
16	Commercial arsenic oxid (dissolved arsenic acid)	.....	.....	66.10	.....	66.10

[1] Determined by the A. O. A. C. method for Paris green.

Attention is called to the wide variation in the data obtained for water-soluble arsenious oxid in the different samples of arsenious oxid. This is undoubtedly due to differences in the size and structure of the crystals present in the samples tested.

Traces of arsenious oxid (0.008 per cent) and nitric acid (0.02 per cent) were found in the commercial sample of arsenic acid (No. 16).

[3] Italic numbers in parentheses refer to literature cited.

All samples of commercial arsenic acid are likely to contain traces of arsenious oxid and nitric acid. Arsenic acid solutions containing from 56 to 66 per cent of arsenic oxid have a specific gravity of from 1.8 to 2. Solid arsenic acid containing from 75 to 80 per cent of arsenic oxid has recently been placed on the market.

BASES USED IN PREPARING ARSENICALS.

The oxids of lead, zinc, calcium, and magnesium are the bases most used in manufacturing arsenicals. Litharge is the commercial lead oxid and lime the commercial calcium oxid. Zinc oxid (ZnO) and lead oxid (PbO), ordinarily employed in the manufacture of zinc arsenite and lead arsenate, are more expensive than calcium oxid (CaO) (in the form of lime) and magnesium oxid (MgO) used in manufacturing calcium arsenate and magnesium arsenate. Table 2 gives the results of the analyses of the five bases and the copper oxid (CuO) and barium hydroxid ($Ba(OH)_2$) which were used in this investigation.

TABLE 2.—*Composition of bases in arsenicals.*

Sample No.	Material analyzed.	Moisture.	Oxid.	Carbon dioxid (CO_2).	Undetermined material, by difference.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
11	Lime (laboratory)	6.54	84.00 (CaO)	9.02	0.44
12	Lead oxid (laboratory)	.00	99.13 (PbO)	Trace.	.87
20	Lead oxid (commercial)	.02	97.88 (PbO)	1.64	.46
22	Zinc oxid (commercial)	.17	100.00 (ZnO)	.00	.....
63	Magnesium oxid (laboratory)	.99	77.16 (MgO)	21.89	.....
65	Copper oxid (laboratory)	.00	98.75 (CuO)	.10	1.15
67	Barium hydroxid (laboratory)	14.58	66.73 (BaO)	14.91	3.78

ACID LEAD ARSENATES.

F. C. Moulton, chemist for the Massachusetts gypsy moth committee, is credited with the discovery in 1892 of the insecticidal properties of lead arsenate. The use of arsenate of lead as an insecticide, first recommended in October, 1893 (*21*), has greatly increased during the past few years. Thirty-one United States patents for its production have been issued.

The principal lead arsenate is acid lead arsenate ($PbHAsO_4$), an acid salt, so-called because of the presence of hydrogen (H) in its molecule. It has the following theoretical composition, As_2O_5 (33.13 per cent), PbO (64.29 per cent), and water of constitution (2.58 per cent).

In the early procedure for preparing acid lead arsenate, solutions of lead acetate or of lead nitrate were precipitated by sodium hydrogen arsenate (Na_2HAsO_4). The tendency is to produce acid lead arsenate when lead nitrate is used and the more basic form when the acetate is used. McDonnell and Smith (*27*) obtained acid lead arsenate of practically theoretical composition by precipitating lead nitrate or lead acetate by an excess of monopotassium arsenate. A method frequently employed in manufacturing this arsenate is to mix arsenic acid (H_3AsO_4) and litharge (PbO) in the presence of a small amount of nitric acid. Other processes, however, are used. The fact that acid lead arsenate is a comparatively stable compound and is but

slightly soluble in water, offers an explanation as to why it burns foliage only very slightly when properly applied. McDonnell and Graham (*26*) found that long-continued exposure to constantly changing water brings about decomposition, both lead and arsenic being dissolved, the arsenic, however, at a relatively greater rate, leaving the residue more basic than the original acid lead arsenate. According to McDonnell and Smith (*27*), the specific gravity of acid lead arsenate crystals is 6.05.

The chemical data on 10 samples of powdered lead arsenates and on 9 samples of paste lead arsenate, the latter being dried in the laboratory before analysis, are reported in Table 3. Of the powdered arsenate samples 1 apparently was a basic lead arsenate and 9 were acid lead arsenates. Of the paste lead arsenate samples, 1 apparently was a basic lead arsenate and 8 were acid lead arsenates. These samples, which were obtained from various manufacturers in this country, include most of the leading brands. The results of the analyses, therefore, are representative of the composition of the commercial lead arsenates on the market in 1916.

TABLE 3.—*Composition of powdered and paste commercial lead and calcium arsenates.*

Sample No.	Material analyzed.	Moisture.	Arsenic oxid (As_2O_5).		Oxid.	Carbon dioxid (CO_2).	Water of constitution and impurities by difference.[1]
			Total.	Water-soluble.			
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	Powdered acid lead arsenate	0.32	30.86	0.31	64.88 (PbO)	0.54	3.40
2	do	1.43	31.55	.24	62.95 (PbO)	.15	3.92
13	do	.21	32.29	.32	64.23 (PbO)	.....	3.27
14	do	.17	32.00	.30	63.42 (PbO)	.....	4.41
35	do	.30	31.24	.38	64.35 (PbO)	.....	4.11
38	do	.14	32.47	.45	64.29 (PbO)	.....	3.10
39	do	.20	32.93	.67	63.92 (PbO)	.....	2.95
40	do	2.06	32.76	.45	63.70 (PbO)	.....	1.48
70	do	.45	31.59	.22	63.00 (PbO)	.....	4.96
28	Powdered basic lead arsenate	.35	24.80	.43	72.23 (PbO)	.....	2.62
3	Paste acid lead arsenate, dried	.10	31.95	.34	64.57 (PbO)	Trace.	3.38
4	do	.12	32.30	.42	64.50 (PbO)	.....	3.08
29	do	.19	30.38	.53	65.21 (PbO)	.....	4.22
43	do	.11	32.07	.11	65.01 (PbO)	.....	2.81
44	do	.11	33.17	.22	63.82 (PbO)	.....	2.90
47	do	.11	32.51	.22	64.67 (PbO)	.....	2.71
48	do	.22	33.09	.67	63.41 (PbO)	.....	3.28
49	do	.12	32.98	1.73	63.13 (PbO)	.....	3.77
21	Paste basic lead arsenate, dried	.11	23.00	.50	73.99 (PbO)	.....	2.90
6	Paste calcium arsenate, dried	.28	43.35	.70	38.86 (CaO)	2.74	14.77
7	Powdered calcium arsenate	1.58	43.35	.38	44.08 (CaO)	1.83	9.16
24	do	1.33	49.40	2.74	40.57 (CaO)	.98	7.72
32	do	.31	41.82	.22	42.61 (CaO)	1.64	13.62
34	do	9.56	38.16	1.92	37.38 (CaO)	4.34	10.56
56	do	7.71	39.19	.55	42.79 (CaO)	4.04	6.27
57	do	11.30	40.49	.08	44.03 (CaO)	1.05	3.13
58	do	.99	47.83	.25	46.16 (CaO)	1.70	3.32
59	do	6.07	45.37	2.32	41.48 (CaO)	2.43	4.65

The results in Table 3 show that in most cases the chemical composition of the commercial samples of acid lead arsenates closely approaches the theoretical composition. The manufacture of lead arsenate has become standardized to such an extent that different batches, or "runs," of the product vary but little from the theoretical figures. Acid lead arsenates are sold in both dry and paste form, the paste containing usually from 45 to 50 per cent of water.

The two most important determinations to be made on lead arsenates are the total arsenic oxid and the water-soluble arsenic oxid. The total arsenic oxid of an acid lead arsenate usually varies from 31 to 33 per cent, and the water-soluble arsenic oxid is less than 0.3 per cent in a good grade of commercial acid lead arsenate.

Robinson and Tartar (*37*) reported analytical results on commercial lead arsenates and described various tests used to determine the forms in which the lead and the arsenic are combined, as well as the extent to which these forms exist in such substances.

In acid lead arsenate the ratio by weight of arsenic oxid to lead oxid is theoretically 1 to 1.94. According to the results of the analysis (Table 3), however, this ratio is somewhat higher in commercial lead arsenates, showing that a slight excess of lead oxid (litharge) had been used in their manufacture in order to make sure that no uncombined arsenic acid would be left in the product. A small amount of carbon dioxid, which had been introduced in the litharge, was found in the acid lead arsenates tested. This is of no practical significance. In all but three of the powdered samples the moisture content was less than 0.35 per cent. The water of constitution of acid lead arsenates is theoretically 2.58 per cent. The results by difference show differences slightly greater than the theoretical figures, but in no case are they of any magnitude. The percentages of arsenic oxid and lead oxid, together with the low percentage of water-soluble arsenic oxid, indicate that the commercial acid lead arsenates examined were good and stable products.

BASIC LEAD ARSENATE.

The early investigators recognized "basic," or "sub," arsenate of lead and applied the term "neutral lead arsenate" to $PbHAsO_4$, which is the present commercial acid lead arsenate. They also applied the term "neutral lead arsenates" to lead pyroarsenates, which are not commercial products, and therefore will not be discussed here. McDonnell and Smith have printed a report on pyroarsenates (*27*). As a result of another investigation on basic lead arsenates, these authors (*28*) report the existence of a basic arsenate having optical and crystallographic properties similar to those of mimetite, from the analytical data apparently hydroxy mimetite, containing one molecule of water of crystallization. One or two manufacturers of insecticides sell, generally on special order, what is commercially called "T. P." arsenate.

Basic lead arsenate may be prepared as follows: Produce basic lead acetate by the action of acetic acid on lead or lead oxid, usually litharge. Then mix it with arsenic acid, thus forming basic lead arsenate. Basic lead arsenate may also be made by the reaction of sodium arsenate, litharge, and nitric acid, or by the action of ammonia on acid lead arsenate. It has the following theoretical composition: As_2O_5 (23.2 per cent), PbO (75 per cent), and water of constitution and crystallization (1.8 per cent). The specific gravity of this substance was found by McDonnell and Smith (*28*) to be 6.86.

Only two samples (Table 3, Nos. 28 and 21) of commercial basic lead arsenate (a powder and a paste) were secured on the market. While these showed somewhat greater variations from the theoretical than did the acid lead arsenates, both are relatively pure compounds.

They have essentially the same composition except for the presence of water in the paste.

CALCIUM ARSENATES.

It is not known who made the first sample of calcium arsenate. Pickering (*31*) in 1907 stated that calcium arsenate had already been used in the United States as an insecticide. He gave the proportions of a calcium salt and an arsenate to be united in preparing calcium arsenate, recommending the use of an excess of lime in order to produce a calcium arsenate with all the arsenic precipitated and therefore containing no appreciable amount of water-soluble arsenic.

As many of the early commercial samples of calcium arsenate contained excessive amounts of water-soluble arsenic, frequent scorching of foliage resulted from its use, thus retarding its general introduction. Since 1907, many experiments to devise a method for making a commercial calcium arsenate have been performed. It is now being produced by many American manufacturers and its sale is constantly increasing. The quality of the commercial product has been much improved during the past few years, but its course of manufacture has not yet been standardized as has that of lead arsenate.

Dicalcium arsenate ($CaHAsO_4(H_2O)$) contains theoretically 28.3 per cent of calcium oxid and 58 per cent of arsenic oxid. It breaks down easily in water, yielding a large quantity of water-soluble arsenic and is not suitable for commercial spraying purposes.

Calcium meta-arsenate ($Ca(AsO_3)_2$) was prepared according to directions obtained from C. M. Smith, of the insecticide and fungicide laboratory. Because of its extreme insolubility, it can not be used for insecticidal purposes.

All the commercial calcium arsenates are made more basic than tricalcium arsenate; that is, the molecular ratio of calcium oxid to arsenic oxid is 4 to 1, rather than 3 to 1. The additional lime is used in their manufacture in order to produce compounds relatively free from water-soluble arsenic.

The following simple method of preparing calcium arsenate commercially, as outlined by Haywood and Smith (*18*), calls for the direct mixing of calcium hydroxid and arsenic acid, the only by-product being water: Slake the lime to a smooth paste by using from 3 to 3½ times as much warm water (by weight) as lime, and allow it to stand until the lime is completely slaked. Then mix it, add the cold arsenic-acid solution at room temperature as rapidly as possible, and stir the mixture well until the liquid becomes alkaline to phenolphthalein. Lastly, filter, dry, and grind the resulting compound.

The lime and arsenic acid should be mixed in such proportion that the actual weight of calcium oxid used will be equivalent to that of the arsenic oxid employed. This method produces a reasonably light (bulky) material, which is easily pulverized. The finished product should contain approximately 44 per cent of calcium oxid, from 40 to 42 per cent of arsenic oxid, and from 14 to 16 per cent of water and impurities, which approaches the ratio, 4 CaO: 1 As_2O_5. The excess of lime is used to keep any soluble calcium arsenate from remaining in the product.

The analytical results on nine samples of calcium arsenate are recorded in Table 3. Samples 6, 24, and 34 were not strictly commercial products, but were made by the manufacturers as an experiment. Sample 24 contains a higher percentage of arsenic than the strictly commercial samples. Samples 6, 24, and 34 have a lower lime content than the six commercial samples analyzed, and it is probable that a portion of their arsenate is in the form of dicalcium arsenate. The somewhat large amount of carbon dioxid found in all of the samples of calcium arsenate comes from the lime, which is always carbonated to a certain extent. The water of the calcium arsenates varies more than that of the lead arsenates. Analyses of samples 56 and 57 showed, respectively, 11.75 per cent and 12.35 per cent loss on ignition, 0.35 and 0.5 per cent of ferric oxid and aluminum oxid, 0.51 per cent and 0.74 per cent of magnesium oxid, and 0.62 per cent and 0.51 per cent of sodium oxid. Sample 56 contained 0.35 per cent of antimony oxid.

Lovett (*23*) in 1918 reported a high water-soluble arsenic content in samples of commercial calcium arsenate. Since then the amount of water-soluble arsenic in commercial calcium arsenate has been reduced, as shown in Table 3. Lovett (*24*) in 1920 published graphs showing the chemical features of calcium arsenate, apparently based on the percentages of lime or on the ratio of lime to arsenic oxid in the calcium arsenates. No consideration seems to have been given to the percentages of total and water-soluble arsenic oxid which are the generally recognized criteria for judging the quality of calcium arsenates chemically.

Robinson (*35*), who tested the solubility of calcium arsenates in water containing lime, reported that the lime prevents the arsenic oxid from becoming soluble. He also studied the action of carbon dioxid on calcium arsenates and found that carbonic acid has a solvent action upon the calcium arsenates. Patten and O'Meara (*30*) made a series of tests on the amount of soluble arsenic oxid obtained from calcium arsenate in water containing carbon dioxid and in water free from carbon dioxid. From their results, which showed a great increase of soluble arsenic oxid when carbon dioxid was present, they concluded that the burning of foliage, when calcium arsenate is applied, is due to the arsenic made soluble by the carbon dioxid of the air.

The commercial calcium arsenates contain approximately one-third more lime than is required by tricalcium arsenate. They contain a higher percentage of total arsenic oxid than the lead arsenates, but they should be manufactured more cheaply per unit of arsenic oxid because of the low cost of the base (CaO).

Coad and Cassidy (*10*) have recommended that calcium arsenate for dusting cotton should contain not less than 40 per cent of arsenic oxid and not more than 0.75 per cent of water-soluble arsenic oxid, and that it should occupy a volume of from 80 to 100 cubic inches a pound.

PARIS GREEN.

Paris green, originally used as a paint pigment, is said to have first served as an insecticide in the western United States. It is a compound of arsenic, acetic acid, and copper, known as aceto-arsenite of copper. The theoretical composition of Paris green is copper oxid

(31.39 per cent), arsenious oxid (58.55 per cent), and acetic anhydrid (10.06 per cent).

The manufacture of Paris green,[4] which has become standardized, may be briefly described thus: Solutions of soda ash (commercial anhydrous sodium carbonate) and arsenious oxid are first heated together, forming sodium arsenite. Crystalline copper sulphate is dissolved in warm water in a separate container. The sodium arsenite mixture is poured into a mixing tank, the copper sulphate solution is added, and the mixture is stirred. Acetic acid is added, and after a little stirring the olive-colored mixture becomes green. The Paris green is washed with water, after which it is allowed to settle and all the water that can be drained off is so removed. This washing should be repeated as often as necessary to remove practically all the sodium sulphate. The Paris green is then dried. The dried product is passed through a "breaker" and finally through a fine sieve or a bolting machine. The "tailings" are mixed with the next batch of Paris green. The finely divided Paris green is now ready to be placed in containers.

The color of Paris green varies with the details of manufacture and the degree of fineness of the product. The composition of Paris green on the market ranges from 54 to 57 per cent of total arsenious oxid, from 1.5 to 4.5 per cent of water-soluble arsenious oxid, and from 29 to 30 per cent of copper oxid.

Haywood (*17*) stated that the impurities in Paris green include small amounts of sand, sodium sulphate, and arsenious oxid, and also that the soluble arsenic in Paris green produces scorching of foliage.

Paris green, when of a high grade, breaks down to some extent when water is added, but when it has been improperly prepared much more soluble arsenic is yielded on treatment with water. Avery and Beans (*2*) found that high-grade Paris green was slowly attacked by water and that the rate of decomposition was increased by grinding to a very fine powder and suspending in water. They also found that the presence of carbon dioxid in the water increased the rate of decomposition. There are two sources of the soluble arsenic in Paris green, (*a*) the soluble arsenic originally present in the sample, and (*b*) the arsenic made soluble by water and carbon dioxid after the material has been applied. The admixture of lime with Paris green when used as a spray lessens its scorching properties. Analysis of a typical Paris green (sample 64) is given in Table 4.

MISCELLANEOUS COMMERCIAL ARSENICALS.

Analyses of samples of several miscellaneous arsenicals which were tested against insects are given in Table 4.

[4] Details of the manufacture of Paris green are given in 45 Ann. Rept. Sec. Mass. State Board Agr. (1897), p. 357.

Zinc arsenite is made by heating together arsenious oxid, zinc oxid, and water. It is sold only as a powder. The arsenious oxid content of the two samples (Nos. 23 and 33) analyzed is approximately the same as the average arsenic oxid content of the calcium arsenates on the market. The water-soluble arsenious oxid figures are a little higher than the results for the best grade of lead or calcium

TABLE 4.—*Composition of miscellaneous arsenicals.*

Sample No.	Material analyzed.	Moisture.	Total arsenious oxid (As_2O_3).	Total arsenic oxid (As_2O_5).	Water-soluble arsenious oxid (As_2O_3).
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
23	Commercial zinc arsenite	0.15	41.49	.....	0.52
33	.....do	.06	42.54	.....	.85
64	Commercial Paris green	.53	55.09	.....	1.94
36	Commercial calcium and lead arsenates	3.15	.....	46.17	.....
8	Commercial calcium and lead arsenates plus calcium carbonate	1.03	.....	21.95	.....
62	Commercial magnesium arsenate	2.96	.....	33.60	.....
71	Laboratory barium arsenate	.29	.....	30.93	.....
74	Laboratory copper and barium arsenate	1.78	.....	14.36	.....
73	Laboratory aluminum arsenate	10.29	.....	37.65	.....
31	Commercial sodium arsenate	3.40	.....	45.16	.....
41	.....do	6.32	.....	59.80	.....
25	Laboratory sodium arsenate	37.54	.....	37.99	.....
26	Laboratory potassium arsenate	.35	.....	59.39	.....
90	Commercial London purple	6.41	31.10	.25	1.41

Sample No.	Material analyzed.	Water-soluble arsenic oxid (As_2O_5).	Oxid.	Carbon dioxid (CO_2).	Undetermined.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
23	Commercial zinc arsenite	.....	56.30 (ZnO)	.....	2.06
33	.....do	.....	56.46 (ZnO)	.....	.94
64	Commercial Paris green	.....	8.29 (CuO) .17 (CaO)	.....	35.92
36	Commercial calcium and lead arsenates	1.14	5.98 (PbO) 37.45 (CaO)	1.50	5.75
8	Commercial calcium and lead arsenates plus calcium carbonate	.53	46.37 (CaO) 2.11 (PbO)	23.23	5.31
62	Commercial magnesium arsenate	1.56	34.32 (MgO)	.55	28.57
71	Laboratory barium arsenate	.21	64.96 (BaO)	1.33	2.49
74	Laboratory copper and barium arsenate	.90	11.18 (CuO) 47.47 (BaO)	.13	25.08
73	Laboratory aluminum arsenate	.72	16.84 (Al_2O_3)	.....	35.22
31	Commercial sodium arsenate	45.16	45.76 (Na_2O)	.....	5.68
41	.....do	59.80	27.66 (Na_2O)	.....	6.22
25	Laboratory sodium arsenate	37.99	19.35 (Na_2O)	.....	5.12
26	Laboratory potassium arsenate	59.39	36.00 (K_2O)	.....	4.26
90	Commercial London purple	.25	34.88 (CaO)	4.37	22.99

arsenates. For more detailed information, the publication of Schoene (*44*) on zinc arsenite should be consulted.

Magnesium arsenates.—It is theoretically possible to prepare ortho, meta, and pyroarsenates of magnesium in the same manner as the corresponding arsenates of lead. Practically twice as much magnesium, calculated as magnesium oxid, was found in the sample analyzed as is needed to combine with the arsenic oxid present. Patten and O'Meara (*30*) give analytical results on a magnesium arsenate containing 32.13 per cent of arsenic oxid and 1.25 per cent of water-soluble arsenic oxid. They found 41.7 per cent of the total arsenic to be soluble in water containing carbon dioxid. A commercial magnesium pyroarsenate analyzed by them had a low

solubility in water and yielded only 3.01 per cent of arsenic oxid soluble in water saturated with carbon dioxid.

London purple, originally a by-product in the manufacture of aniline dyes, is now made directly to a limited extent. It consists of arsenite of lime and arsenate of lime, with the addition of a dye. Table 4 gives the composition of the material used in the investigation. The analyses of four additional samples showed the following variations: Arsenious oxid, 18.30 to 29.38 per cent; arsenic oxid, 0.07 to 11.49 per cent; water-soluble arsenious oxid, 0.48 to 5.30 per cent; and water-soluble arsenic oxid, 0.07 to 2.46 per cent. One sample showed 24.91 per cent of calcium oxid, 2.70 per cent of magnesium oxid, and 11.25 per cent of ferric oxid and silicon dioxid. London purple, therefore, is of uncertain composition and contains varying amounts of water-soluble arsenious oxid and arsenic oxid. On account of its variable character and its tendency to burn foliage, the addition of lime is recommended when it is used as a spray.

Calcium and lead arsenates combined (samples 36 and 8) were analyzed and tested on insects. The demand for a mixed calcium and lead arsenate is limited. It is held by some that lead arsenate adheres to foliage better than calcium arsenate, so that the presence of a little lead arsenate in the mixture increases the adhesive properties. The use of calcium carbonate in the mixture reduces the percentage of arsenic present and permits the product to be sold more cheaply.

Sodium arsenate was formerly on the market in two grades, a 45 per cent and a 65 per cent arsenic oxid product. During the past three or four years it has been difficult to obtain sodium arsenate in commercial quantities. In preparing sodium arsenate containing 45 per cent of arsenic oxid, nitrate of soda (Na_2NO_3), arsenious oxid (As_2O_3), sodium carbonate (Na_2CO_3), and salt (NaCl) are roasted together. In preparing the 65 per cent grade the salt is omitted. The two commercial samples (Nos. 31 and 41) correspond to these two grades, although sample 41 contains about 60 per cent of arsenic oxid. Sample 31 contains 28.44 per cent of sodium chlorid, sample 41, 6.14 per cent, and sample 25, 0.096 per cent. Calculating the results for these two samples and for sample 25 (prepared in the laboratory) to a moisture-free basis, sample 25 contains 60 per cent, sample 31 about 47 per cent, and sample 41 about 64 per cent of arsenic oxid. All the arsenic present in sodium arsenate is water soluble. Sodium arsenate is sometimes added to Bordeaux mixture to produce a combined fungicide and insecticide. The excess lime of Bordeaux combines with the arsenic oxid of the sodium arsenate, forming insoluble calcium arsenate. The amount of sodium arsenate added and the amount of the excess lime of the Bordeaux are the factors which determine whether all of the soluble sodium arsenate is converted into the insoluble calcium arsenate.

Potassium arsenate.—Sample 26 is a laboratory product containing 59.39 per cent of arsenic oxid, all of which is soluble in water. No commercial samples of potassium arsenate are now available.

MISCELLANEOUS EXPERIMENTAL ARSENICALS.

The analytical results on three samples of lead arsenates and four samples of calcium arsenates made in the laboratory are given in Table 5.

TABLE 5.—*Composition of lead and calcium arsenates prepared in the laboratory.*

Sample No.	Material analyzed.	Moisture.	Arsenic oxid (As_2O_5).		Lead oxid (PbO).	Calcium oxid (CaO).	Carbon dioxid (CO_2).	Water of constitution and impurities, by difference.
			Total.	Water-soluble.				
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
17	Acid lead arsenate	0.02	33.09	0.19	63.80	.....	.....	3.09
68	.....do	.10	33.25	.00	63.67	.....	.....	2.98
18	Basic lead arsenate	.06	23.40	.27	74.66	.....	.....	1.88
45	Calcium meta-arsenate	.03	79.63	Trace.	.....	18.45	0.00	1.89
46	Monocalcium arsenate	.23	69.09	61.67	.....	19.92	.10	10.66
42	Tricalcium arsenate	1.06	52.05	.46	.....	40.07	.96	5.86
69	.....do	2.30	42.84	.17	.....	44.89	5.73	4.24

Lead arsenates.—The two samples of acid lead arsenate (Nos. 17 and 68) contained percentages of arsenic oxid very close to the theoretical (33.11). They were prepared by mixing lead nitrate and arsenic acid, according to the procedure of McDonnell and Smith (*27*). The percentage of lead oxid in the two samples is a little lower than the theoretical. Basic lead arsenate (sample 18) was prepared by the action of ammonia on acid lead arsenate. There is slightly more arsenic oxid and slightly less lead oxid in this sample than is called for by the theoretical figures. Both the acid and basic lead arsenates were made from pure lead oxid and crystallized arsenic acid; consequently they are extremely pure.

Calcium arsenates.—A calcium meta-arsenate ($Ca(AsO_3)_2$) (sample 45) was prepared according to directions obtained from C. M. Smith of the insecticide and fungicide laboratory. The theoretical percentage of arsenic oxid for such a product is 80. No moisture or carbon dioxid was present in the sample, as the product had been ignited. Although high in arsenic oxid, the product is so insoluble that its insecticidal properties would undoubtedly be low. A monocalcium arsenate ($CaH_4(AsO_4)_2$) (sample 46) was also prepared according to Smith's directions. Its theoretical composition is as follows: Arsenic oxid (71.4 per cent), calcium oxid (17.41 per cent), and water of crystallization and water of constitution (11.19 per cent). This compound is very soluble in water and can not be considered a commercial possibility as an insecticide. Two samples of tricalcium arsenate were prepared. The composition of sample 42 approached the theoretical composition of tricalcium arsenate ($Ca_3(AsO_4)_2.2H_2O$) as determined by Robinson (*35*), 38.7 per cent of calcium oxid, 53 per cent of arsenic oxid, and 9.3 per cent of moisture and water of constitution. Sample 69 was prepared by using equal weights of lime and arsenic oxid, which gave a compound with an excess of lime, having slightly more than 4 equivalent parts of calcium oxid to 1 part of arsenic oxid, and containing but 0.17 per cent of water-soluble arsenic oxid. Calcium arsenate of this composition was recommended by Haywood and Smith (*18*) as suitable for commercial manufacture.

Barium arsenate seems to have been used first by Kirkland (*20*) in 1896. The next year Kirkland and Burgess (*21*) tested barium arsenate against certain insects. Smith (*48*) in 1907 also used a barium arsenate. Its preparation is not described by any of these investi-

gators. A sample of barium arsenate (sample 71, Table 4) was prepared by adding a solution of arsenic acid to a solution of barium hydroxid with constant stirring. The details were as follows: Dissolve 546 grams of barium hydroxid ($Ba(OH)_2.8H_2O$), containing 240 grams of barium, in 3 liters of water to which 300 cubic centimeters of commercial arsenic acid, containing 0.4 gram of arsenic oxid per 1 cubic centimeter, has been added. After this mixture has been thoroughly stirred, the precipitated barium arsenate soon settles. Then wash the precipitate several times by decantation, filter it on a Büchner filter, dry and pulverize it, and finally pass it through a 100-mesh sieve. The theoretical composition of tribarium orthoarsenate ($Ba_3As_2O_8$) is as follows: Barium (59.7 per cent) and arsenic oxid (33.32 per cent); that is, the ratio of arsenic oxid to barium is 1 to 1.8. The ratio for the sample made in the laboratory was 1 to 1.9, showing the presence of a slight excess of barium. Its insecticidal value is discussed on page 38.

Copper barium arsenate mixture (sample 74, Table 4) was made as follows: A solution containing 360 grams of copper sulphate was mixed with 275 grams of arsenic oxid. No precipitate resulted. A dilute solution of barium chlorid was added and then barium hydroxid until the solution was but slightly acid. The mixture of copper and barium arsenate and barium sulphate was then thoroughly stirred and allowed to settle. The precipitate was washed several times by decantation and then was separated by filtering on a Büchner filter. The precipitate was finally dried, ground, and passed through a 100-mesh sieve. Its adhesive and fungicidal properties have not been tested, but its insecticidal powers are discussed on pages 38 to 46.

Aluminum arsenate (sample 73, Table 4) was prepared by mixing a solution of aluminum sulphate with arsenic acid. The precipitate was washed, filtered, and dried. The insecticidal results of this product are discussed on pages 38 to 42.

Copper arsenate was prepared by mixing a solution of copper sulphate with arsenic acid and then adding ammonia. The percentage of water-soluble arsenic oxid in this product was so high that no additional tests were made with the sample.

Zinc arsenate has been prepared by several investigators. The sample prepared in this study was made by mixing a solution of zinc chlorid with arsenic acid. Its physical properties did not seem to warrant further study.

COMBINATIONS OF ARSENICALS WITH FUNGICIDES AND OTHER MATERIALS.

In order to reduce the cost of spraying, various combinations of arsenicals with fungicides are frequently made. The arsenicals are also mixed with other substances, like glue and casein, to increase the length of time the arsenicals will adhere to the foliage or fruit.

While some of these combinations are frequently made, very little exact knowledge as to the chemical changes which take place in them is available. Accordingly, an investigation was undertaken to obtain information on the changes which occur in some of the important combinations involving arsenicals. One pound of powdered acid lead arsenate per 50 gallons of water is recommended as satisfactory for most commerical spraying. Acid lead arsenate at this rate and other arsenicals in corresponding amounts, depending on their arsenious or arsenic oxid contents, were used in the tests.

Thus amounts of the arsenicals containing equivalent percentages of arsenious or arsenic oxid were taken in each case.

In all the tests the mixtures of the arsenicals and other material were agitated in flasks by rotating in a water bath which was maintained at a constant temperature of 35° C. All were made in triplicate, but only the average figures are reported in the tables. The soluble arsenic (that found in the filtrates) was determined by the modified Gutzeit test (*47*) or by the Gooch-Browning method (*1*).

ARSENATES AND LIME-SULPHUR.

Ruth (*38*) made a study of the chemical changes resulting when acid lead arsenate and lime-sulphur were mixed. He found (*a*) a decrease of lime and sulphur in the solution, (*b*) an increase of thiosulphate sulphur in the solution and in the residue, (*c*) an increase of sulphite in the solution, (*d*) formation of lead sulphid, and (*e*) the formation of a compound containing arsenic and sulphur, but insoluble in the lime-sulphur solution. Robinson (*35*), after agitating mixtures of lead arsenate and lime-sulphur for three days, allowed them to settle and then poured off the clear liquid. He found that 25 per cent of the lime and more than 35 per cent of the sulphur had been precipitated and that 5 per cent of the arsenic had become soluble. Robinson and Tartar (*37*) tested mixtures of lime-sulphur and lead arsenates (4.8 grams of arsenate per 1,000 cubic centimeters of lime-sulphur, diluted 1 to 30). When basic lead arsenate was used little change occurred, but when acid lead arsenate was used an increase of soluble arsenic and a decrease of total soluble sulphur and polysulphid sulphur resulted. They concluded that the efficiency of the lime-sulphur had been reduced 25 per cent, and that the arsenic rendered soluble might injure foliage. Fields and Elliott (*15*) present data showing that less than five parts per million of arsenic oxid by weight was made soluble when solutions of lime-sulphur were mixed with either acid or basic lead arsenates.

In the present investigation standard commercial lime-sulphur solution was diluted (1 to 30) with recently boiled and cooled distilled water. Control flasks (500 cubic centimeters volume), completely filled with this diluted solution, were securely closed with stoppers and paraffin and agitated for 1-hour and 91-hour periods. Other flasks, filled with the diluted solution of lime-sulphur, to each of which 1.2 grams of powdered acid lead arsenate (sample 39) had been added, were similarly treated. Series of three flasks were removed, and the solutions were filtered immediately on removal from the bath. The results obtained with lead arsenate are given in Table 6.

TABLE 6.—*Composition of lime-sulphur solution and of the filtrates from mixtures of lead arsenate or calcium arsenate and lime-sulphur solution.*

Material analyzed.	After having been shaken for—	Composition (grams per 500 cubic centimeters).					
		Total lime (CaO).	Total sulphur (S).	Sulphid sulphur (S).	Thio-sulphate sulphur (S).	Sulphate sulphur (S).	Arsenic oxid (As_2O_5).
SERIES 1:							
Lime-sulphur solution	1 hour	1.9680	4.9430	4.5190	0.1960	0.0035	0.0002
	91 hours	2.0520	4.9290	4.5060	.2030	.0069	.0002
Filtrates from mixtures of lead arsenate and lime-sulphur solution	1 hour	1.8050	4.4770	4.1620	.2020	.0029	.0270
	19 hours	.....	4.2670	4.0450	.1990	.0055	.0205
	43 hours	.....	4.2560	3.9080	.1980	.0036	.0199
	91 hours	1.8030	4.2790	3.7110	.1970	.0076	.0200
SERIES 2:							
Lime-sulphur solution	1 hour	1.9800	5.2500	4.7800	.3200	.0089	.0002
	21 hours	1.9900	5.2500	4.7500	.3200	.0099	.0002
	5 days	2.0400	5.2000	4.7000	.3300	.0077	.0003
Filtrates from mixtures of calcium arsenate and lime-sulphur solution	1 hour	2.0400	5.1000	4.7500	.3200	.0089	.0008
	21 hours	2.0600	5.0500	4.6800	.3300	.0087	.0005
	5 days	1.9600	5.1000	4.7000	.3600	.0108	.0010

Using the analytical data on the lime-sulphur solution as controls, the analytical results on filtrates from a mixture of lead arsenate and lime-sulphur solution show the following: (*a*) The total lime in solution was reduced 10 per cent after having been shaken for either 1 hour or 91 hours; (*b*) the total sulphur in solution was reduced 9.5 per cent after 1 hour and 14 per cent after 19, after 43, and after 91 hours; (*c*) the sulphid sulphur was reduced 8 per cent after 1 hour and 18 per cent after 91 hours; (*d*) the thiosulphate sulphur remained unchanged after each period; (*e*) the sulphate sulphur increased slightly, although the same increase was observed in the control; and (*f*) 5.2 per cent of the total arsenic oxid of the lead arsenate used was rendered soluble. From these results, it is apparent that chemical changes have occurred. The mixture is therefore chemically incompatible.[5] Some of the sulphur in lime-sulphur solution probably united with the lead of the lead arsenate and produced lead sulphid, which could be seen as black particles in the mixture. The arsenic oxid group, liberated by the decomposition of the lead arsenate, was then free to combine with the lime in the lime-sulphur solution, probably forming calcium sulph-arsenate. The formation of insoluble tricalcium arsenate took place only to a limited degree.

Robinson (*34*) in examining mixtures of calcium arsenates and lime-sulphur found that no reaction took place in such mixtures. His tests with "dry lime-sulphur" mixed with calcium arsenate showed the presence of no soluble arsenic, but those with "soluble sulphur" mixed with calcium arsenate showed that it was present. Lovett (*24*) also reported that no changes take place when calcium arsenate is mixed with lime-sulphur solution.

Experiments similar to the lead arsenate tests were performed, using calcium arsenate (sample 57) in place of the acid lead arsenate. A series of 500 cubic centimeter flasks were filled with lime-sulphur solution diluted 1 to 30. Nine of the flasks were used as controls; to each of the others 1 gram of calcium arsenate was added. The solutions were agitated for periods of 1 hour, 21 hours, and 5 days. They were immediately filtered and the filtrates were tested.

[5] The term "compatible" is here used only in the chemical sense.

The data given in Table 6 (series 2) show that no detectable changes took place when calcium arsenate and lime-sulphur were mixed. The small amount of arsenic found in the filtrates was the water-soluble arsenic originally present in the calcium arsenate and amounted to 0.2 per cent of the total arsenic oxid in the calcium arsenate.

In brief, it is evident that chemical changes take place when acid lead arsenate and lime-sulphur are mixed. This mixture is therefore incompatible chemically. When calcium arsenate is mixed with lime-sulphur no soluble arsenic is formed in the case of high-grade products. Therefore this arsenate, when mixed with lime-sulphur, would seem to be a satisfactory insecticide. Field experience, however, shows that it often injures the foliage sprayed.

Such a mixture is chemically compatible and has been recommended by Quaintance and Siegler (*32*), Sanders (*40*), and others, who, however, do not claim that it is always free from burning properties.

No experiments with basic lead arsenate and lime-sulphur were performed. Bradley (*5*), in 1909, used basic lead arsenate in combination with lime-sulphur, and found 0.28 and 0.43 per cent of soluble arsenic. He considered that there was no danger of the formation of excessive amounts of soluble arsenic in such mixtures. Bradley and Tartar (*6*), who used both acid and basic lead arsenates in combination with lime-sulphur, found eight times more soluble arsenic with acid lead arsenate than with basic lead arsenate. Both forms of lead arsenate were more soluble in saline water than in pure water. Alkaline carbonates exerted a decomposing action, especially on acid lead arsenate.

ARSENATES AND BORDEAUX MIXTURE.

Fields and Elliott (*15*) stated that very little soluble arsenic is present when Bordeaux mixture is combined with lead arsenate. They found in both the acid and the basic lead arsenates only from 1 to 3 parts of soluble arsenic per million.

Since combinations of arsenicals with Bordeaux mixture are frequently made, it was considered important to determine whether or not chemical changes take place in these combinations. Tests were therefore conducted in which 4–3.67–50 Bordeaux mixture was prepared, dried, and passed through a 100-mesh sieve. Four-gram samples of the dry Bordeaux were placed in each of a series of 300 cubic centimeter flasks and to each flask were added portions of one of the four arsenicals in the following amounts: 0.8 gram of acid lead arsenate (sample 39); 0.667 gram of calcium arsenate (sample 57); 0.69 gram of sodium arsenate (sample 25); and 0.47 gram of Paris green (sample 64). Mixtures of the various arsenicals alone and of Bordeaux alone in distilled water were prepared and tested under the same conditions as the mixtures of the arsenicals and Bordeaux. The flasks were agitated at a temperature of 35° C. for periods of 1 hour, 1 day, and 3 days. The mixtures were filtered immediately and the filtrates were tested for copper by the colorimetric test with potassium ferrocyanid (*12*) and for lead by the lead sulphid color test as used by W. D. Lynch, of the insecticide and fungicide laboratory. The analytical data are given in Table 7.

No copper was found in any of the filtrates. The filtrates from the acid lead arsenate Bordeaux mixtures contained the following per-

centages of the total lead present in the sample: For the one-hour period, 3 per cent; for the one-day period, 7 per cent; and for the three-day period, 7.6 per cent. The results for water-soluble arsenic in the combinations are lower than those for water-soluble arsenic in the arsenicals alone. It is evident that the excess lime of the Bordeaux combined with part of the soluble arsenic present in the arsenates, forming insoluble calcium arsenate.

The results show that Bordeaux mixture and the arsenates of lead and calcium, as well as Paris green, are compatible, that a soluble arsenate, such as sodium arsenate, may be used in quantities large enough to act as an insecticide in combination with ordinary Bordeaux mixture, and that the excess lime of the Bordeaux will combine with the soluble arsenic to form insoluble calcium arsenate.

ARSENATES AND KEROSENE EMULSION.

As kerosene emulsion is occasionally used in combination with acid lead arsenate and may be used with calcium arsenate, a series of experiments was undertaken to determine whether detectable chemical changes take place in these combinations.

A kerosene emulsion was prepared according to the following directions:[6] One liter of commercial kerosene oil and 1 ounce of sodium fish-oil soap in water were mixed, and the resulting emulsion was diluted to 10 liters.

A series of 300 cubic centimeter flasks were filled with this emulsion and 0.8 gram of acid lead arsenate (sample 39) or 0.667 gram of calcium arsenate (sample 57) was added to each of the flasks, with the exception of the control flasks. Mixtures of the arsenates alone and of the emulsions alone were used for controls. The mixtures were agitated at 35° C. for periods of one hour, one day, and three days. They were filtered immediately and the filtrates were tested for arsenic. The average figures only are recorded in Table 7.

TABLE 7.—*Soluble arsenic in filtrates from combinations of arsenicals with Bordeaux mixture and with kerosene emulsion.*

Sample No.	Material analyzed.	Total arsenic (As) in sample taken.	Soluble arsenic (As) found after standing for—			Percentage of total arsenic (As) found soluble after standing for—		
			1 hour.	1 day.	3 days.	1 hour.	1 day.	3 days.
		Grams.	*Grams.*	*Grams.*	*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*
25	Sodium arsenate	0.1709	.....	.....	0.1650	.....	.....	96.55
64	Paris green	.1938	.....	.....	.0066	.....	.....	3.41
57	Calcium arsenate	.1753	.....	.....	.00034	.....	.....	0.20
39	Acid lead arsenate	.1709	.....	.....	.0048	.....	.....	2.81
61	Bordeaux mixture	.....	.....	.....	.00006	.....	.....	.....
—	Sodium arsenate (25) plus Bordeaux (61)	.1709	0.00095	0.00001	.00001	0.56	0.00	.00
—	Paris green (64) plus Bordeaux (61)	.1938	00113	.00053	.00046	.58	.27	.24
—	Calcium arsenate (57) plus Bordeaux (61)	.1753	.00003	.00005	.00000	.02	.03	.00
—	Acid lead arsenate (39) plus Bordeaux	.1709	.00051	.00030	.00018	.30	.18	.11
—	Calcium arsenate (57) plus kerosene emulsion	.1753	.0018	.0095	.0122	1.03	5.42	6.96
—	Acid lead arsenate (39) plus kerosene emulsion	.1709	.0332	.0768	.0740	19.43	44.94	43.30

[6] Taken from U. S. Dept. Agr. Farmers' Bull. 958, p. 28.

The amount of arsenic made soluble was much larger when acid lead arsenate was combined with kerosene emulsion than when calcium arsenate was combined with it. The same amount of arsenic was rendered soluble in one day as in three days in the case of the acid lead arsenate. When calcium arsenate was used, 1.5 per cent more of the total arsenic was made soluble the third day than the first day. It is evident that the lead and the lime of the arsenates combined with the fatty acids to produce soaps, leaving the corresponding amounts of arsenic in a soluble condition. The results show that less decomposition occurred in the case of calcium arsenate mixed with kerosene emulsion than in the case of acid lead arsenate and kerosene emulsion. Both mixtures are chemically incompatible.

ARSENATES AND FISH-OIL SOAP.

Combinations of acid lead arsenate with fish-oil soap are sometimes made. Because of the large quantity of calcium arsenate now being manufactured, it seemed advisable to test combinations of calcium arsenate and of acid lead arsenate with fish-oil soap in order to determine how much arsenic might be made soluble.

Fish-oil soap solutions of two strengths, 1 and 2 pounds of soap per 50 gallons, were prepared. The fish-oil soap was the same kind as that used in making the kerosene emulsion. A series of 300 cubic centimeter flasks were filled with the soap solution. No arsenical was added to some of the flasks which were used as controls, but 0.8 gram of acid lead arsenate (sample 39) or 0.667 gram of calcium arsenate (sample 57) was added to the others. A one-day period was taken for agitating the solutions, because the results with kerosene emulsion showed that in one day the reactions were practically complete for the lead arsenate and much retarded in the case of the calcium arsenate.

TABLE 8.—*Arsenic rendered soluble on combining lead or calcium arsenates with fish-oil soap.*

Sample No.	Material analyzed.	Arsenic (As) present in sample taken.	Arsenic (As) rendered soluble after standing for 1 day.	
		Grams.	*Grams.*	*Per cent.*
57	Calcium arsenate [1]	0.1753	0.0003	0.17
39	Acid lead arsenate [2]	.1717	.0032	1.86
—	Calcium arsenate plus fish-oil soap (1 pound to 50 gallons)	.1753	.0503	28.69
—	Acid lead arsenate plus fish-oil soap (1 pound to 50 gallons)	.1717	.1475	85.90
—	Calcium arsenate plus fish-oil soap (2 pounds to 50 gallons)	.1753	.0667	38.05
—	Acid lead arsenate plus fish-oil soap (2 pounds to 50 gallons)	.1717	.1703	99.18

[1] Calcium arsenate at the rate of 0.93 pound per 50 gallons.
[2] Lead arsenate at the rate of 1.11 pounds per 50 gallons.

The results obtained (Table 8) follow the trend of the results secured with kerosene emulsion (Table 7) in that they show that more arsenic was rendered soluble when acid lead arsenate was used than when calcium arsenate was used. They also show that the greater the quantity of fish-oil soap used the larger the amount of soluble arsenic formed. All of the arsenic was made soluble when acid lead arsenate was mixed with the soap at the rate of 2 pounds per 50 gallons. The lead soaps are more readily formed than the

lime soaps, for which reason more arsenic was left in a free or soluble form when acid lead arsenate was used than when calcium arsenate was used. Based on the results of chemical analyses, both of these mixtures are incompatible.

ACID LEAD OR CALCIUM ARSENATES AND NICOTINE SULPHATE SOLUTIONS.

Mixtures of acid lead arsenate and of calcium arsenate with a solution of nicotine sulphate were prepared and analyzed. A 1–800 dilution of a 40 per cent solution of nicotine sulphate was made. In the first series 500 cubic centimeter flasks were filled with this dilute nicotine sulphate solution and 1.2 grams of acid lead arsenate (sample 39) or 1 gram of calcium arsenate (sample 57), containing 13 per cent of free calcium oxid, was added to each of the flasks, with the exception of the controls. Results of the analyses of the lead and calcium arsenates used are given in Table 3. After agitating the different solutions for periods of one hour, one day, and three days they were immediately filtered and the filtrates were analyzed for arsenic and nicotine. Nicotine was determined by the official silicotungstic acid method (*1*). A second series of tests, using two commercial calcium arsenate samples (Nos. 32 and 59) and a pure tricalcium arsenate prepared by C. M. Smith, was made. Sample 32 contained 9.99 per cent, sample 59, 5.23 per cent, and sample 464 no free calcium oxid. In this series 0.6 gram of the calcium arsenate was placed in each of a series of 300 cubic centimeter flasks, which were made to volume with the dilute nicotine sulphate solution. These solutions were agitated for one hour and for three days.

TABLE 9.—*Results of combining acid lead arsenate or calcium arsenate with nicotine-sulphate solutions.*

Material analyzed.	Soluble nicotine after agitating for—			Soluble arsenic oxid (As_2O_5) after agitating for—		
	1 hour.	1 day.	3 days.	1 hour.	1 day.	3 days.
500 cubic centimeter volume tests:	*Grams.*	*Grams.*	*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*
Nicotine-sulphate solution	0.2748	.....	0.2820	0.00	.....	0.00
Acid lead arsenate (39) plus nicotine sulphate	.2748	0.2789	.2763	.45	0.34	.60
Calcium arsenate (57) plus nicotine sulphate	.2778	.2815	.2815	.44	.52	.50
Acid lead arsenate (39)	.0000	.0000	.0000	.60	.....	.....
Calcium arsenate (57)	.0000	.0000	.0000	.30	.....	.....
300 cubic centimeter volume tests:						
Nicotine-sulphate solution	.1740	.....	.....	.00	.....	.00
Calcium arsenate (32) plus nicotine sulphate	.1750	.....	.....	1.15	.....	1.09
Calcium arsenate (59) plus nicotine sulphate	.1760	.....	.....	11.04	.....	11.50
Calcium arsenate (464) plus nicotine sulphate	.1740	.....	.....	10.39	.....	11.86
Calcium arsenate (32)	.....	.....	.....	.27	.....	.27
Calcium arsenate (59)	.....	.....	.....	2.09	.....	2.22
Calcium arsenate (464)	.....	.....	.....	3.34	.....	3.57

The results (Table 9) show that acid lead arsenate (sample 39) when combined with nicotine sulphate gives no increase of soluble arsenic and that the amount of soluble nicotine is not altered. This mixture is therefore chemically compatible.

When calcium arsenates are combined with nicotine sulphate solutions, soluble arsenic oxid may be produced, depending on the sample of calcium arsenate used and on the quantity of nicotine sulphate present in the mixture. The percentage of soluble arsenic oxid will be low if there is enough excess lime in the calcium arsenate to combine with the SO_4 of the nicotine sulphate. If sufficient excess lime is not present, the SO_4 combines with some of the CaO of the calcium arsenate, liberating soluble arsenic oxid. Calcium arsenate (sample 57) contained 13.16 per cent of free calcium oxid, and when combined with nicotine sulphate only 0.5 per cent of free arsenic oxid was found. Calcium arsenate (sample 32) contained 9.99 per cent of free calcium oxid, and when combined with nicotine sulphate 1.15 per cent of soluble arsenic oxid was found.

When the free lime in the calcium arsenates was low or absent entirely there was a marked rise in the percentage of soluble arsenic oxid. For example, sample 59, containing 5.23 per cent of free calcium oxid, and sample 464, containing no free calcium oxid, gave practically 12 per cent of soluble arsenic oxid. Sample 6 (3.68 per cent free calcium oxid) and sample 58 (9.06 per cent free calcium oxid) gave, respectively, 6.67 and 2.28 per cent of soluble arsenic oxid after being agitated for 1 hour with nicotine sulphate solution in the proportions given. These mixtures, therefore, are chemically incompatible, and the only way that such a combination should be made is to use a high-grade calcium arsenate containing at least 10 per cent of excess calcium oxid and using a proportion of nicotine sulphate no higher than that used in these tests.

The lime of calcium arsenate decomposes the nicotine sulphate, leaving free nicotine, but does not change the amount of nicotine present. The results given in Table 9 show that the percentage of soluble nicotine was not altered by the presence of calcium arsenates.

A few tests made in the insecticide and fungicide laboratory in which free nicotine solution was mixed with acid lead arsenate or with calcium arsenate showed that these combinations were chemically compatible. Results obtained on combining nicotine sulphate solutions with Bordeaux mixture were reported by Safro (*39*) and Wilson (*52*), who claimed that such mixtures were compatible.

PHYSICAL PROPERTIES OF ARSENICALS.

A commercial calcium arsenate and a commercial acid lead arsenate were selected for a series of tests on the adhesive properties of these substances on sprayed foliage, which was extended over three seasons (1917, 1918, and 1919). For each 50 gallons of water 1 pound of powdered acid lead arsenate or an equivalent amount of calcium arsenate, based on the arsenic oxid content, was used. The sprays were applied to potato and apple leaves with a power sprayer. At various periods after the sprays had been applied leaves were gathered for analysis. The leaves were dried and samples of approximately 5 grams each were digested with nitric and sulphuric acids and analyzed for arsenic by the modified Gutzeit (*47*) method. The results (Table 10) by this method do not warrant in all cases the expression to the degree of accuracy which the figures may imply, but this is the common way of expressing results where small amounts of a substance are present.

TABLE 10.—*Arsenic on potato and apple leaves sprayed with lead or calcium arsenates.*

Year and locality.	Spray used.	Average number of samples.	Arsenic (As) found.	
			Per square meter of leaf surface.	On dry leaves.
1917.	POTATO LEAVES.		*Milligrams.*	*Parts per million.*
Washington, D. C.	Acid lead arsenate	7	5	140
Do.	Calcium arsenate	8	3	50
Presque Isle, Me.	Acid lead arsenate	2	80	1,460
Do.	Calcium arsenate	2	56	1,270
Greenwood, Va.	Acid lead arsenate	2	16	50
Do.	Calcium arsenate	2	19	70
1918.				
Washington, D. C.	Acid lead arsenate	3	.....	170
Do.	Calcium arsenate	3	.....	60
Greenwood, Va.	Acid lead arsenate	2	.....	180
Do.	Calcium arsenate	2	.....	270
1919.				
Arlington, Va.	Acid lead arsenate	5	.....	260
Do.	Calcium arsenate	5	.....	210
1917.	APPLE LEAVES.			
Greenwood, Va.	Acid lead arsenate	2	40	510
Do.	Calcium arsenate	2	9	120
1918.				
Greenwood, Va.	Acid lead arsenate	4	.....	130
Do.	Calcium arsenate	4	.....	260

The results of the tests for all three years show an average of 286 parts per million of arsenic on the dry leaves receiving the lead arsenate spray and an average of 219 parts per million of arsenic on the dry leaves receiving the calcium arsenate spray. The 1917 and 1919 results show that a larger percentage of arsenic of acid lead arsenate adhered to the leaves than of the arsenic of the calcium arsenate. The 1918 results are practically the same for the two arsenates.

Lime was used with certain of the arsenates in some of the 1918 tests (Table 11). Potato vines were sprayed with a commercial calcium arsenate and a commercial acid lead arsenate alone and with the addition of lime to each. Zinc arsenite and calcium meta-arsenate were used without the addition of lime. Two calcium arsenates, one with a molecular ratio of 3 CaO to 1 As_2O_5 and the other with one of 4 to 1, were tested, with and without the addition of lime. In these two cases both 2 ounces and 4 ounces of lime per 10 gallons of spray were used. The arsenious or arsenic oxid contents of the sprays were made the same in all cases, with the exception of calcium meta-arsenate. From the data in Table 11 it is evident that the lime was of no advantage in increasing the amount of arsenic adhering to the leaves.

TABLE 11.—*Arsenic on potato leaves sprayed with arsenicals with and without the addition of lime.*[1]

Sample No.	Material used.	Total arsenic oxid (As_2O_5) in dry arsenical.	Arsenical used per 10 gallons.	Arsenic (As) on dry leaves.
		Per cent.	*Ounces.*	*Parts per million.*
24	Calcium arsenate	49.40	2	240
24A	Sample 24 plus lime (2 ounces)	49.40	2	340
40	Acid lead arsenate	32.76	3½	530
40A	Sample 40 plus lime (2 ounces)	32.76	3½	580
23	Zinc arsenite	[2] 41.49	2½	540
86	Calcium meta-arsenate	79.60	2½	830
87	Calcium arsenate	55.00	2	290
87A	Sample 87 plus lime (2 ounces)	55.00	2	270
87B	Sample 87 plus lime (4 ounces)	55.00	2	290
88	Calcium arsenate	42.80	2½	360
88A	Sample 88 plus lime (2 ounces)	42.80	2½	280
88B	Sample 88 plus lime (4 ounces)	42.80	2½	380

[1] Equal percentages of As_2O_3 and As_2O_5 were used for all the sprays.
[2] As_2O_3.

During the season of 1920 potato plants were sprayed at Arlington, Va., using (*a*) dry acid lead arsenate, (*b*) dry "suspender" [7] acid lead arsenate, (*c*) zinc arsenite, and (*d*) Paris green. The sprays were made to contain the same percentage of arsenious or arsenic oxid and were applied four times during the season, using a power sprayer. Nine duplicate sets of 50 leaves each were collected on the same days throughout the season from each plot of the various sprayed vines. These leaves (900 in all from each plot receiving a different spray) were analyzed for arsenic, with the following average results, expressed as parts of arsenic per million of dried potato leaves: Paris green, 155; "suspender" acid lead arsenate, 195; zinc arsenite, 203; and acid lead arsenate, 210.

The physical properties of arsenicals have been studied to some extent since the time they were first prepared, but no complete study has been reported. This may be due in part to the difficulties encountered in measuring those physical properties which contribute toward making a satisfactory product for dusting or spraying. Wilson (*53*) in 1919 gave data on the burning, suspensibility, and adhesiveness of Paris green, zinc arsenite, acid and basic lead arsenates, and calcium arsenate.

A series of tests was performed, using commercial powdered arsenicals (Table 12), to obtain comparative data on the apparent density and suspensibility of these products. The apparent density of a powder here described is based on the number of grams occupying a volume of 1,000 cubic centimeters and the suspensibility on the volumetric readings of 30 grams of powder which had settled after having been shaken for one minute with approximately 500 cubic centimeters of water and having stood for 10 and for 60 minutes.

[7] "Suspender" lead arsenate is a trade name applied to a powdered lead arsenate containing some added organic substance for the purpose of keeping the arsenate in suspension when mixed with water.

TABLE 12.—*Physical properties of commercial powdered calcium and lead arsenates and zinc arsenite.*

Sample No.	Material examined.	Total arsenic oxid (As_2O_5) in powders.	Apparent density.[1]	Suspension properties after standing for[2]—	
				10 minutes.	60 minutes.
		Per cent.	*Grams.*	*Cubic centimeters.*	*Cubic centimeters.*
59	Calcium arsenate	45.37	254	245	200
58	....do	47.83	257	188	115
97	....do	40.38	364	365	145
98	....do	41.40	365	380	120
24	....do	49.40	422	170	140
57	....do	40.49	532	245	57
56	....do	39.19	567	170	71
85	Acid lead arsenate	31.89	247	230	167
39	....do	32.93	249	270	132
83	....do	31.50	284	110	123
84	....do	32.90	306	265	135
38	....do	32.47	369	146	90
82	....do	32.75	747	88	60
23	Zinc arsenite	[3] 41.49	355	165	77

[1] Weight of powder occupying a volume of 1,000 cc. without being jarred.
[2] Based on volumetric readings of 30 grams of powder, shaken with 500 cc. of water and allowed to stand.
[3] Arsenious oxid (As_2O_3).

In Table 12 the calcium and acid lead arsenates are arranged according to their apparent densities, the lightest ones first. The lightest powders usually remained suspended for the longest time (60-minute test) and the heavy powders settled most rapidly. More than 90 per cent of all the arsenicals tested passed a 40-mesh sieve after having been shaken for five minutes. These results are of no value and therefore are not given. It is believed that the fineness of powdered arsenicals, which are generally amorphous, can not be correctly determined by this test, since fine powders pack in a 40-mesh sieve. The fineness of relatively coarse arsenicals, such as arsenious oxid, can be determined by sieving.

Microscopical examinations of the various arsenicals were made. A large number of samples of powdered calcium and acid lead arsenates and one of zinc arsenite were blown from a dust gun. These dusts, collected on six or more microscopic slides placed at varying distances from the dust gun, were photographed. Then, using a high-power lens of the microscope, drawings were made by the aid of the camera lucida which made possible the determination of slight differences in the size of particles but did not give satisfactory information on the dusting or spraying properties of these products.

Several samples of powdered lead arsenate and Paris green, examined under a magnification of 100 diameters, appeared to be amorphous. The samples of calcium arsenate contained a few small crystals, although the samples on the whole appeared to be largely without crystalline shapes. Four samples of arsenious oxid were examined under the microscope. Samples 19 and 27 consisted chiefly of small octahedral crystals; sample 37 contained somewhat larger crystals.

COMPARATIVE TOXICITY OF ARSENICALS.

RESULTS OF PREVIOUS INVESTIGATIONS.

CALCIUM ARSENATE.

Bedford and Pickering (*3*) and Smith (*48*) appear to have been the first to use calcium arsenate as an insecticide. In 1907 all three of these men tried it as a substitute for lead arsenate. Bedford and Pickering found it practically as efficient as acid lead arsenate on fruit trees in England. Against the army worm in New Jersey, however, Smith did not find it satisfactory.

Between 1907 and 1912, calcium arsenate apparently was not further tested as an insecticide, but during the seasons of 1912, 1913, and 1914, the office of fruit insect investigations of the Bureau of Entomology, United States Department of Agriculture, began to test it, as a result of which a commercial calcium arsenate was put on the market. Since 1915 the use of this arsenate in the field has steadily increased. In 1914 a commercial calcium arsenate in combination with lime-sulphur gave very satisfactory control of the codling moth (*45*).

Scott (*46*), who, during the seasons of 1913 and 1914, used calcium arsenate, states that for spraying apple and shade trees, it may be used with the same degree of efficiency and safety as acid lead arsenate.

Sanders (*40*), using acid lead and calcium arsenates of equal arsenic contents, found the lead salt slightly superior in killing power, but the calcium salt more desirable for use with sulphid sprays.

Sanders and Kelsall (*42*) state that when calcium arsenate is used alone it may under some conditions burn foliage, but that when used in combination sprays with Bordeaux mixture or lime-sulphur, it is as safe as any known arsenical. In sodium sulphid sprays it is much the safest of all arsenicals. It adheres fairly well to foliage and remains in suspension.

Coad (*9*) used various arsenicals, as dusts, against cotton boll weevils. He found acid lead arsenate much more toxic than basic lead arsenate and a high-grade calcium arsenate still more effective. Coad and Cassidy (*10* and *11*) recommend a high-grade calcium arsenate above all other arsenicals for controlling the cotton boll weevil, and they enumerate some of the physical and chemical properties that such an arsenical should have.

Ricker (*33*), testing poison baits against grasshoppers, determined that calcium arsenate, used in direct competition with Paris green and crude arsenious oxid, gave equally good results.

BARIUM ARSENATE.

Barium arsenate seems to have been used first by Kirkland (*20*), who tested it in Massachusetts against the larvæ of the gypsy moth, fall webworm, and *Datana ministra*, securing satisfactory results in each case. Kirkland and Burgess (*21*) say:

> The experiments with barium arsenate in 1896 gave so good results that we were hopeful that this insecticide would prove superior to lead arsenate. Its killing effects on larvæ in confinement are certainly superior to those of arsenate of lead. In the field spraying operations it was found that the poison did not adhere to the foliage for a sufficiently long time to kill the larvæ.

Smith (*48*) did not find barium arsenate satisfactory against one species of army worm.

Brittain and Good (*7*) used barium arsenate in 1917 against the apple maggot, but did not recommend it because of its tendency to burn the foliage.

MISCELLANEOUS SPRAY MIXTURES.

Kirkland and Burgess (*21*) determined in field experiments on the gypsy moth that acid lead arsenate is slightly better than basic lead arsenate.

Wilson (*51*) reported that zinc arsenite killed tent caterpillars (*Malacosoma erosa* and *M. pluvialis*) more quickly and stayed in suspension better than the basic lead arsenate. The basic lead arsenate, while slow in its action, finally killed the insects. The same arsenic content was not used for both sprays. Lime-sulphur mixed with arsenicals retarded the action of the arsenicals. Lime-sulphur used alone was not of much value as a stomach poison.

Robinson and Tartar (*36*) conducted tests with tent caterpillars (*M. pluvialis*) on sprayed foliage in an open part of an insectary, using an equal arsenic content. The acid lead arsenate killed more quickly than did the basic lead arsenate which, however, although slow, proved satisfactory because it killed all the caterpillars tested.

Tartar and Wilson (*50*), also using tent caterpillars, determined that acid lead arsenate (2–200) was more efficient than the basic form (2–100). The acid lead arsenate had an arsenic content of about 33 per cent, while the basic form had one of only 25 per cent.

Sanders and Brittain (*41*), reporting tests on the toxic value of certain arsenicals, both alone and in combination with fungicides, against the brown tail moth, tent caterpillar, cankerworm, tussock moth, and fall webworm in the field, report that calcium arsenate is inferior to both acid and basic lead arsenates, and that barium arsenate is still more inferior. Basic lead arsenate is inferior to acid lead arsenate in all combinations except with Bordeaux mixture. They think that Bordeaux mixture does not inhibit the action of the basic form as much as it does that of the other arsenicals used.

Lovett and Robinson (*24* and *25*) used the tent caterpillar (*M. pluvialis*) throughout their experiments to determine the toxic values and killing efficiency of the arsenates. Instead of examining all the larvæ daily to determine the exact number dead, they counted the dead ones that dropped daily from the sprayed foliage in the laboratory. These men also carried on preliminary field experiments with calcium arsenate. They summarize their results as follows:

> Lead hydrogen [acid lead] arsenate has a higher killing efficiency at a given dilution than either calcium or basic lead arsenate. It requires a longer period of time to kill the nearly mature caterpillars than the small forms. All of the arsenic devoured by the insects in feeding upon sprayed foliage is not assimilated, but a portion passes through the intestinal tract in the excrement. The percentage amount of the arsenic assimilated depends upon the arsenate used; lead hydrogen arsenate was assimilated readily and most of the arsenic was retained in the tissues while much of the basic lead arsenate was found in the excrement. It requires approximately 0.1595 milligram of arsenic pentoxid to kill 1,000 small tent caterpillars, and approximately 1.84 milligram of arsenic pentoxid to kill 1,000 nearly mature tent caterpillars, irrespective of the particular arsenate used as a spray.

Howard (*19*), experimenting with the spotted cucumber beetle in the field, used equal amounts (by weight) of several arsenicals. The average mortality on the fifth day, based upon the results of two seasons' work, is as follows: Zinc arsenite, 24 per cent; acid lead arsenate, 17 per cent; Paris green, 16 per cent; Bordeaux-lead arsenate, 14 per cent; and calcium arsenate, 1 per cent.

Sanders and Kelsall (*43*) give comparative figures for the toxicity of several arsenicals. On the basis of one-half pound of metallic arsenic to 100 gallons of liquid, they obtained the following percentages of dead fall webworms on the eighth day: Sodium arsenate, 52; Paris green, 72; acid lead arsenate, 36; zinc arsenite, 60; calcium arsenate, 44; and white arsenic (As_2O_3), 60. On the same arsenic-content basis, but with the addition of Bordeaux mixture (10–10–100) to the spray materials, they obtained the following percentages of dead tussock-moth caterpillars on the eighth day: Sodium arsenate, 60; Paris green, 64; calcium arsenate, 48; and white arsenic, 60.

Wilson (*53*), using five arsenicals against the potato beetle in the field and laboratory, presents their rates of toxicity graphically as follows: Paris green, 80 per cent; zinc arsenite, 65 per cent; acid lead arsenate, 60 per cent; calcium arsenate, 50 per cent; and basic lead arsenate, 20 per cent. He did not use the same arsenic content in any two of them.

EXPERIMENTAL WORK.

In comparing the toxicities of the various arsenicals, fed to several species of insects, equal percentages of the two oxids of arsenic (As_2O_3 and As_2O_5) were used in the spray mixtures.

PREPARATION OF SPRAY MIXTURES.

Suspensions or solutions of each of the arsenicals used were prepared on the basis of the presence of 0.076 gram of arsenious or arsenic oxid per 100 cubic centimeters of distilled water. This proportion is at the rate of 1 pound of dry or 2 pounds of paste acid lead arsenate to 50 gallons of water, it being assumed that 32 per cent is the average arsenic oxid content of a dry acid lead arsenate. On the basis of equal percentage, the mixtures made by using arsenious oxid contained 16.2 per cent more metallic arsenic than did those containing arsenic oxid. Each mixture, however, had either an arsenious or arsenic oxid content of 0.076 per cent. All the laboratory samples used in 1919 and 1920 were pulverized and passed through a 100-mesh sieve before being mixed with water, but the commercial samples were used as purchased. When properly prepared, the arsenical mixtures were placed in clean mason jars having rubbers and tops. Each jar was then thoroughly shaken to dissolve, if possible, and to distribute the arsenical, and subsequently the mixtures were sprayed on foliage which was eaten by insects.

APPLICATION OF SPRAY MIXTURES.

In all, seven species of insects were tested: Silkworms (*Bombyx mori* L.), two species of fall webworms (*Hyphantria cunea* Dru. and *H. textor* Harr.), and tent caterpillars (*Malacosoma americana* Fab.), belonging to Lepidoptera; the Colorado potato-beetle larvæ (*Leptinotarsa decemlineata* Say), belonging to Coleoptera; grasshoppers

(mostly *Melanoplus femur-rubrum* De G.), belonging to Orthoptera; and honeybees (*Apis mellifica* L.), belonging to Hymenoptera. An atomizer was used in all the spraying experiments.

Silkworms.—Silkworm larvæ were fed leaves treated as follows: Mulberry leaves were sprayed with the various mixtures, the control leaves being sprayed with tap water only. After having been dried in the air the leaves were cut into small strips which were then placed in small wire-screen cages. An effort was made to put approximately the same quantity of food in each cage, so that a rough comparative estimate of that consumed could be made. In 1919 about 50 normal silkworms in the second instar (varying in length from 7 to 12 millimeters, with an average of 10 millimeters, and not ready to molt) were put in each cage, but in 1920 silkworms in the third instar (18 to 30 millimeters long, average 25 millimeters) were employed. Counts were made daily except on Sundays, the cages being cleaned and treated food being renewed at the same time. No disease was noticed among these larvæ.

Webworms.—The webs were collected in the fields from a variety of plants on Monday. At the laboratory these webs containing webworms were kept in large cages with a small amount of food until Tuesday noon, when the larvæ, which were then very hungry, were well mixed according to size (all instars but first one). Tuesday morning approximately the same quantity of mulberry foliage was placed in each of several wide-mouthed bottles containing water. It was then sprayed, and, when dry, a bottle with contents was placed in a large battery jar, 8 inches in diameter by 12 inches high. Tuesday afternoon approximately the same number of webworms were placed in each jar, and thereafter the sprayed food was renewed daily. Thus by starting each set of experiments on the same day of the week, the days (Sundays) on which no records were taken always fell on the fifth, twelfth, and nineteenth days of the tests. Very little disease or parasitism was noticed among these larvæ.

Tent caterpillars.—The tents, collected in the fields on wild cherry trees, were handled in the same manner as the webs of webworms. Sprayed wild cherry foliage was placed in the jars daily and counts were made daily. Owing to the prevalence of the "wilt," or polyhedral disease, it was necessary to test these larvæ while in the earliest instars.

Potato-beetle larvæ.—Collected on potato plants, these larvæ were placed in cheesecloth cages, 9 inches square by 12 inches high. They were so well mixed before being placed in the cages that each cage contained about the same number in the various instars. Sprayed potato-plant foliage was given to them daily. Parasitism was common only in the last instar.

Grasshoppers.—The fourth, fifth, and sixth (adults) instars caught in the fields were tested in the cheesecloth cages. Having been unable to use the foregoing spray mixtures, bran mash, mixed with some of the same powdered arsenicals, served as food. Using Paris green (sample 64, containing 55.09 per cent As_2O_3) as a standard, and the regular formula [8] as a basis, a modified formula was derived, whereby a pint of poisoned bran mash containing each arsenical to

[8] Bran, 25 pounds; Paris green, 1 pound; lemons or oranges, 6; molasses, 2 quarts; and water, from 2 to 4 gallons.

be tested was prepared. A temporary preservative was added to the mash. The poisoned mash was so prepared that each pint had an arsenic content of 1.08 per cent. The grasshoppers were fed daily. Parasitism was common, causing a high daily mortality among the controls. The temporary preservative in the control food seems to have increased the mortality about 4 per cent.

Honeybees.—To obtain bees of practically the same age for insecticidal purposes, the brood chamber of a hive was moved 30 feet from the old stand. On the following day all the old bees had returned to the old stand, leaving only young workers (nurse bees and wax generators), the brood, and the queen in the brood chamber. Fifty of these young workers were placed in each of many screen-wire experimental cases and were fed the spray mixtures, diluted twenty times, in the following manner: One cubic centimeter of a diluted mixture was thoroughly mixed with 4 cubic centimeters of honey in a small feeder which was so covered with wire that the bees could not waste the food. The 50 bees were given 0.038 milligram of arsenic or arsenious oxid. If all consumed equal quantities, each one ate 0.0005 milligram of metallic arsenic when the arsenic oxid form was used, or 0.00057 milligram when the arsenious oxid form was employed. After the bees had eaten the poisoned honey they were given queen cage candy. The number found dead was recorded daily. Great care was taken to see that the bees always had plenty of food.

STATEMENT OF RESULTS.

Amount of food consumed.—Not having had time to calculate accurately the amount of food consumed during all of these tests, an effort was made to estimate it, but this was found possible only with the food eaten by the webworms and tent caterpillars. The amount consumed of the foliage placed daily in each jar of larvæ was estimated in tenths and fractional parts of tenths, if necessary. On the twentieth day the experiments were ended and the total amount of food eaten during this period was used in calculating the amount consumed per larva, counting one-hundredth of each daily feeding as a unit.

Criteria of toxicity.—In order to judge the value of these methods, so that the results obtained by using them can be properly interpreted, the following uncontrollable factors should be mentioned: (*a*) The insects always varied more or less in age and size. (*b*) The immature insects molted irregularly, causing an irregularity in feeding, as insects do not eat during the molting period, which may last from one to three days. (*c*) Disease and parasitism were often discovered several days after the experiments had been started. (*d*) The temperature often varied, causing the caterpillars, which are chiefly night "feeders," to eat less on cool nights than on warm nights. (*e*) Some insects die soon after eating a dose of poison, while others lie "sick" for several days before dying, which causes a great variation in their mortality record. (*f*) The sensitiveness of insects to poisons varies. (*g*) In applying the spray mixtures it was impossible to spray two bunches of foliage in such a manner that equal amounts of arsenicals adhered to all the leaves. Moreover, the metallic arsenic in the arsenites and arsenates varied slightly. No two arsenicals adhere equally well to leaves, and all of them have a tendency to collect in drops, causing an unequal distribution of the poison. Neverthe-

less, this spraying was done more thoroughly than is possible in practical spraying. (*h*) It was often difficult to separate the dead insects from those apparently dead. This was accomplished in a fairly satisfactory manner by placing these insects almost against the globe of an electric light. If they exhibited no signs of life after being subjected for five minutes to the heat from this light they were considered dead. (*i*) In these experiments it was impossible to feed definite amounts of the arsenicals to individual insects. In a very limited way it would be possible to feed insects singly, but it is almost impossible to make them eat definite amounts of poisons. It would be possible to feed definite amounts of arsenicals to individual bees. If they remain isolated singly in cages, however, they live for only a few hours, although when 50 or more are confined in one case they freely feed one another and usually live for 9 or 10 days.

Because of these uncontrollable factors, a large number of insects were used for each individual experiment and the experiments were repeated several times, if possible. The results thus obtained are only comparative and are based on the average time required to kill the insects tested rather than on the absolute single lethal doses required to kill them. It was assumed that the insects ate equal amounts of the poisons, although this may never have been true. In the light of these probable errors it is easy to explain the delayed deaths of many of the insects poisoned and the great variation in their daily mortality.

PRELIMINARY TESTS.

During the summers of 1917 and 1918, many preliminary tests were performed on silkworms, tent caterpillars, and fall webworms. While no conclusive data were obtained, the following indications may be given.

The 14 commercial acid lead arsenates (samples 1, 2, 3, 4, 13, 14, 29, 38, 39, 40, 44, 47, 48, and 49) used showed no important differences in insecticidal properties. All proved efficient. The two basic lead arsenates (samples 21 and 28) did not kill as quickly as did the acid lead arsenates. Only two of the five commercial calcium arsenates (samples 5, 6, 7, 24, and 34) tested proved efficient. The insoluble calcium meta-arsenate (sample 45) prepared in the laboratory had no effect, while the laboratory sample of water-soluble monocalcium arsenate (No. 46) killed quickly. The arsenious oxid samples (Nos. 9, 19, 27, and 37), arsenic oxids (samples 10 and 16), sodium arsenates (samples 25, 31, and 41), potassium arsenate (sample 26), and zinc arsenites (samples 23, 30, and 33) were usually efficient. One of these with a high percentage of water-soluble arsenic, however, was not necessarily more toxic than another with a lower percentage of water-soluble arsenic. The bases—lead oxid, (samples 12 and 20), calcium oxid (sample 11), and zinc oxid (sample 22)—had little effect when used alone. From the insecticidal viewpoint, there seems to be no advantage in combining calcium arsenate and lead arsenate (sample 8). When lime was added to the laboratory sample of calcium arsenate (No. 42) the toxicity seemed to be decreased.

RELATIVE TOXICITY OF COMMERCIAL LEAD AND CALCIUM ARSENATES.

Since the preliminary experiments indicated that the commercial acid lead arsenates do not differ greatly in toxicity, sample 39, one of those first used, was selected as a standard by which to judge the relative toxicity of other spray materials, because its arsenic oxid content (32.93 per cent) approaches most nearly the theoretical content (33.11 per cent).

In order to obtain comparable percentages of toxicity for the three arsenates tested against five species of insects, it was first necessary to place all the daily percentages of mortalities on the same basis. This was accomplished by subtracting the daily mortalities of the control insects fed nonpoisoned food from the daily mortalities of the insects fed sprayed food. Since the daily mortalities on any given day vary too much to serve as a fair percentage of toxicity, the average of the mortalities on the third, sixth, and tenth days have been taken. The records given in Table 13 under the twentieth day show whether or not the insecticides used were efficient. To test the effect of starvation on the insects, other controls without food were used also.

The results reported in Tables 13 to 21 are comparable only when the same combination of data and the same number of sets of insects have been used. Data on the number of sets tested and the variation and average number of insects used for each individual spray material, other than those given in the tables, therefore, are stated. For Table 13 these data are as follows: Silkworms, 1 set (variation 48–52, average 50); webworms (*H. cunea*), 2 sets (619–1224: 864); tent caterpillars, 4 sets (711–1126: 897); potato-beetle larvæ, 3 sets (132–157: 145); and grasshoppers, 3 sets (368–482: 420).

TABLE 13.—*Relative toxicity of commercial lead and calcium arsenates on 5 species of insects, after deducting mortality of control with food, 1919 and 1920.*

Sample No.	Arsenates and controls.	Percentage of insects dead within—											
		3 days.						6 days.					
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Grasshoppers.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Grasshoppers.	Average.
39	Acid lead arsenate	96.0	39.1	53.1	61.5	37.6	**57.5**	100.0	91.7	86.5	72.3	31.1	**76.3**
28	Basic lead arsenate	61.3	8.5	53.6	47.0	33.0	**40.7**	81.6	45.0	88.5	66.2	31.6	**62.6**
5	Calcium arsenate	96.0	12.5	54.3	67.5	63.6	**58.8**	100.0	69.1	89.6	66.9	32.6	**71.6**
7	do	14.3	3.6	49.7	45.6	48.0	**32.2**	28.6	15.6	85.2	47.0	32.6	**41.8**
56	do	59.6	4.3	51.8	54.8	62.4	**46.6**	94.3	33.7	87.6	54.9	32.6	**60.6**
57	do	64.0	1.1	43.9	60.5	61.6	**46.2**	86.0	27.8	82.9	73.3	32.6	**60.5**
58	do	12.5	2.7	45.1	50.6	42.6	**30.7**	18.7	18.7	85.6	70.4	32.6	**45.2**
59	do	72.5	3.8	60.3	57.8	61.0	**51.1**	96.1	42.1	81.4	60.8	32.6	**62.6**
	Control without food	12.2	.0	.4	20.1	.....	.....	61.2	28.6	15.3	43.7	.....	.....
	Control with food	.0	.0	1.9	14.6	35.5	**10.4**	.0	.7	5.5	20.7	67.4	**18.9**

TABLE 13.—*Relative toxicity of commercial lead and calcium arsenates on 5 species of insects, after deducting mortality of control with food, 1919 and 1920*—Continued.

Sample No.	Arsenates and controls.	Percentage of insects dead within—										Average toxicity.	Units of food eaten per insect (estimated), based on webworms (*H. cunea*) and tent caterpillars.
		10 days.						20 days.					
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Grasshoppers.	Average for 4 species.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.		
39	Acid lead arsenate	.....	84.5	87.3	52.5	All.	**81.1**	.....	All.	All.	All.	**71.6**	2.9
28	Basic lead arsenate	96.0	74.8	87.5	47.0	All.	**76.3**	100.0	All.	All.	All.	**59.9**	10.9
5	Calcium arsenate	.....	84.0	87.7	53.7	All.	**81.3**	.....	All.	All.	All.	**70.6**	9.1
7	.....do	30.3	24.4	87.7	40.6	All.	**45.8**	44.9	20.7	All.	All.	**39.9**	66.0
56	.....do	98.1	52.4	86.8	43.8	All.	**70.3**	100.0	49.8	All.	All.	**59.2**	30.8
57	.....do	98.0	50.3	84.7	51.5	All.	**71.1**	100.0	45.7	All.	All.	**59.3**	29.9
58	.....do	22.9	22.2	87.7	53.2	All.	**46.5**	29.2	20.5	All.	All.	**40.8**	69.1
59	.....do	100.0	69.4	86.6	52.3	All.	**77.1**	.....	51.9	All.	All.	**63.6**	18.5
	Control without food	71.5	83.3	79.3	37.4	.....	.....	100.0	All.	All.	34.0	.....	.....
	Control with food	.0	14.4	12.3	42.5	78.3	**17.3**	0.0	41.8	50.5	57.1	**15.5**	100.0

Table 13 shows the following: The average percentages of toxicity of the acid lead arsenate (sample 39) and of one sample of calcium arsenate (sample 5) on five species of insects are practically the same; the percentage of toxicity for another calcium arsenate spray (sample 59) is a little lower; those for two other calcium arsenates (samples 56 and 57) and for basic lead arsenate (sample 28) are practically the same; while those for the remaining calcium arsenates (samples 7 and 58) are very low. Samples 7 and 58 were not efficient against all five species of insects tested. The basic lead arsenate acted much more slowly on the silkworms and webworms than did the acid lead arsenate, but, as a rule, only slightly more slowly on the tent caterpillars, potato-beetle larvæ, and grasshoppers. The quantity of food consumed is inversely proportional to the toxicity, being least for samples 39 and 5 and most for samples 58 and 7. The results in this table also show that starvation had little or no effect on the insects tested, but that the insects really died from the effects of the arsenates.

EFFECT ON TOXICITY OF ADDING LIME TO ARSENICALS.

According to the preliminary experiments conducted in 1917 and 1918, the laboratory sample of calcium arsenate (sample 42) and the same compound plus 0.3 gram of lime (sample 42A) killed 69 per cent and 68 per cent, respectively, of the webworms counted on the twelfth day. When the quantity of lime was doubled (sample 42B) the mortality was 50 per cent, and when it was quadrupled (sample 42C), 40 per cent. In 1919 many other experiments, in which a larger amount of lime was added to every 418 cubic centimeters of another laboratory sample of calcium arsenate, were performed, using silkworms, 1 set (variation 49–53, average 51); webworms (*H. cunea*), 2 sets (538–818: 622); tent caterpillars, 4 sets (785–1021: 943); webworms (*H. textor*), 1 set (181–325: 266); potato-beetle larvæ, 3 sets (290–361: 339); and potato-beetle adults, 1 set (37–41: 39). De-

ducting the mortalities of the controls and basing the average percentages of toxicity on the mortalities of the third, sixth, tenth, and twentieth days, the results for all these insects are: Sample 69, 45; sample 69A (sample 69 plus 0.5 gram lime), 32.7; sample 69B (sample 69 plus 1 gram lime), 29.1; sample 69C (sample 69 plus 2 grams lime), 26.5.

TABLE 14.—*Effect on toxicity of adding lime to arsenicals on 4 species of insects, 1919 and 1920.*

Sample No.	Arsenicals and control.	Percentage of insects dead within—									
		3 days.					6 days.				
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.
39	Commercial acid lead arsenate.	91.0	11.0	18.1	21.0	**35.3**	100.0	72.8	82.2	58.0	**78.3**
39C	Sample 39 plus lime (2 grams)..	69.0	6.3	18.0	14.0	**26.8**	93.0	38.3	81.1	40.0	**63.1**
69	Laboratory calcium arsenate...	32.7	5.4	42.3	12.0	**23.1**	53.8	39.7	91.6	44.0	**57.3**
69C	Sample 69 plus lime (2 grams)..	9.4	1.8	33.3	7.0	**12.9**	15.1	14.4	91.2	23.0	**35.9**
64	Commercial Paris green.....	100.0	30.7	65.7	15.0	**52.8**	.....	85.2	99.0	62.0	**86.6**
64C	Sample 64 plus lime (2 grams)..	57.0	1.8	23.4	8.0	**22.5**	79.0	44.2	86.0	56.0	**66.3**
39	Commercial acid lead arsenate.	.....	20.3	.....	.....	.....	.....	79.0	.....	.....	.....
39L	Sample 39 (leaves sprayed with sample 11 lime).....	.....	20.5	.....	.....	.....	.....	78.7	.....	.....	.....
57	Commercial calcium arsenate..	.....	7.5	.....	.....	.....	.....	30.4	.....	.....	.....
57L	Sample 57 (leaves sprayed with sample 11 lime).....	.....	2.3	.....	.....	.....	.....	12.2	.....	.....	.....
	Control with food.....	.0	.0	.6	.0	.....	.0	.0	8.8	12.0	.....

Sample No.	Arsenicals and control.	Percentage of insects dead within 10 days.				Toxicity for—				Average toxicity.
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.[1]	
39	Commercial acid lead arsenate.....	.....	99.3	100.0	**99.8**	97.0	61.0	66.8	39.5	**66.1**
39C	Sample 39 plus lime (2 grams).....	100.0	82.9	100.0	**94.3**	87.3	42.5	66.4	27.0	**55.8**
69	Laboratory calcium arsenate.....	59.6	66.0	98.8	**74.8**	48.7	37.0	77.6	28.0	**47.8**
69C	Sample 69 plus lime (2 grams).....	22.6	30.2	100.0	**50.9**	15.7	15.5	74.8	15.0	**30.2**
64	Commercial Paris green.....	.....	100.0	100.0	**100.0**	100.0	72.0	88.2	38.5	**74.7**
64C	Sample 64 plus lime (2 grams).....	100.0	99.4	100.0	**99.8**	78.7	48.5	69.8	32.0	**57.2**
39	Commercial acid lead arsenate.....	.....	93.6	.....	.....	.....	64.3	.....	.....	.....
39L	Sample 39 (leaves sprayed with sample 11 lime).....	.....	95.1	.....	.....	.....	64.7	.....	.....	.....
57	Commercial calcium arsenate.....	.....	66.0	.....	.....	.....	34.6	.....	.....	.....
57L	Sample 57 (leaves sprayed with sample 11 lime).....	.....	36.4	.....	.....	.....	17.0	.....	.....	.....
	Control with food.....	.0	2.6	23.1	.....	.....	.....	.....	.....	.....

[1] Based on mortalities for third and sixth days only, because these controls, confined in small cases, lived for only 8.4 days on an average.

In 1920 these experiments were repeated on a larger scale. The following data are not given in Table 14: Silkworms, 2 sets (each of 50); webworms (*H. cunea*), 1 set (variation 136–194: 145); tent caterpillars, 3 sets (198–385: 280); and honeybees, 2 sets (each of 50). The percentages given for samples 69 and 69C are taken from the 1919 results, and should be compared only roughly with the other percentages given in Table 14. Reference to this table shows that

the addition of lime to the three arsenicals employed reduced the toxicity in practically all cases.

There are two possible explanations for the reduction in toxicity due to the addition of lime. The excess lime may unite with the soluble arsenic and prevent it from functioning as a poison. This explanation is supported by practically all the results recorded, providing the excess lime did not decrease the percentage of arsenic in the food or on the leaves eaten. It did not reduce the percentage of arsenic in the poisoned honey, yet the lime in every case caused a decrease in toxicity to honeybees. In the case of the leaf-eating insects, the lime added theoretically reduced the percentage of arsenic on the leaves, because 2 grams of lime were mixed with every gram or less of the arsenical. Consequently, the dried spray material on the leaves would be greatly adulterated and the percentage of arsenic in it would be lowered. To determine the extent of the decrease in the arsenic, many leaves were sprayed with samples 39, 39C, 69, 69C, 64, and 64C. After repeating these experiments three times and analyzing the 18 samples of leaves sprayed, it was found that the addition of lime had reduced the arsenic on the leaves 26.3 per cent, while the excess lime on other leaves similarly sprayed had reduced the average toxicity of the same three arsenicals only 21.1 per cent.

In order to prevent the decrease of arsenic on the leaves, at the same time retaining an excess of lime on them, the following experiments were performed. Many leaves were sprayed, some with acid lead arsenate (sample 39) and others with calcium arsenate (sample 57). When dry, half of each lot was again sprayed with lime (sample 11) (2 grams of calcium oxid in 418 cubic centimeters of water). When all the leaves were dry, half of them were prepared as samples to be analyzed for arsenic and the other half were fed to fall webworms. These experiments were repeated twice, using 8,888 webworms in all. The results in Table 14 show that the lime (sample 39L) did not affect the toxicity of the acid lead arsenate (sample 39), but it (sample 57L) reduced the toxicity of the calcium arsenate (sample 57) 50 per cent. Analyses of the leaves sprayed with samples 39 and 39L showed that the lime reduced the arsenic 18 per cent, while in those sprayed with samples 57 and 57L the arsenic was reduced 29.4 per cent.

EFFECT ON TOXICITY OF ADDING BORDEAUX MIXTURE AND LIME-SULPHUR TO ARSENICALS.

Sanders and Brittain (*41*) reported that Bordeaux mixture and Wilson (*51*) reported that lime-sulphur, when added to arsenical spray mixtures, decrease the killing power of the arsenicals. Many experiments were performed by the writers in 1919 to determine whether or not these statements were true. The following insects were used: Webworms (*H. cunea*), 1 set (variation 102–476, average 241); tent caterpillars, 4 sets (742–1187: 919); and potato-beetle larvæ, 2 sets (130–264:153). After deducting the mortalities of the controls, the average percentages of toxicity of the three species of insects used are as follows: Sample 68 (laboratory sample of acid lead arsenate), 47.1; sample 50 (sample 68 plus lime sulphur), 40.1; sample 69 (laboratory sample of calcium arsenate), 55.6; sample 53 (sample 69

plus Bordeaux mixture), 42.8; sample 51 (sample 69 plus lime-sulphur), 41.8; sample 23 (commercial zinc arsenite), 51.4; and sample 54 (sample 23 plus Bordeaux mixture), 46. From these figures it seems that both Bordeaux mixture and lime-sulphur decreased the toxicities of the arsenicals used. Since silkworms and honeybees refuse to eat food containing lime-sulphur, the experiments in which they were used are not reported. All the other larvæ enumerated ate only about 25 per cent as much food as did the controls, while those that fed on foliage sprayed only with Bordeaux mixture and lime-sulphur ate 83 per cent and 54 per cent, respectively. Neither Bordeaux mixture nor lime-sulphur used alone had much insecticidal value against the insects tested.

In 1920 these experiments were repeated. Different arsenicals were tested, but the Bordeaux mixture (4–3.67–50) and lime-sulphur (1–30) were of the same strengths. The Bordeaux mixture and arsenicals were so mixed that each dry spray material consisted of practically 22 per cent of arsenious or arsenic oxid, and when the necessary amount of water was added, each had an arsenic or arsenious oxid content of 0.076 per cent. Table 15 gives the analytical results on these spray materials before water was added.

TABLE 15.—*Composition of Bordeaux mixture alone and in combination with arsenicals.*

Sample No.	Material analyzed.	Moisture.	Arsenious (As_2O_3) or arsenic (As_2O_5) oxid.		Base.	Carbon dioxid (CO_2).
			Total.	Water-soluble.		
		P. ct.	*P. ct.*	*P. ct.*	*Per cent.*	*P. ct.*
61	Laboratory sample of Bordeaux mixture (4–3.67–50).	0.68	.....	.....	15.90 (CuO) 54.49 (CaO)	3.52
91	Sample 61 plus acid lead arsenate (39).....	.24	22.06	0.12	5.60 (CuO) 18.16 (CaO) 42.52 (PbO)	1.17
92	Sample 61 plus calcium arsenate (57).....	.57	22.30	.26	9.09 (CuO) 53.10 (CaO)	5.29
55	Sample 61 plus sodium arsenate (25).....	15.64	22.16	16.81	6.63 (CuO) 22.70 (CaO)	.....
54	Sample 61 plus zinc arsenite (23).....	.37	23.05	.23	7.07 (CuO) 24.22 (CaO) 31.38 (ZnO)	1.95
30	Commercial Bordeaux and zinc arsenite mixture.	.46	24.33	.38	30.55 (ZnO) 8.92 (CaO)	.56

Table 16 shows the average percentages of toxicity against webworms and tent caterpillars of lead arsenate and of calcium arsenate alone, with Bordeaux mixture, and with lime-sulphur, and of sodium arsenate and zinc arsenite alone and with Bordeaux mixture.

TABLE 16.—*Effect on toxicity of adding Bordeaux mixture and lime-sulphur to arsenicals on four species of insects, 1920.*

Sample No.	Arsenicals and control.	Percentage of insects dead within—									
		3 days.					6 days.				
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.
39	Commercial acid lead arsenate	91.0	11.0	18.1	21.0	**35.3**	100.0	72.8	82.2	58.0	**78.3**
91	Sample 39 plus Bordeaux mixture (61)	78.0	7.4	11.3	12.0	**27.2**	99.0	40.0	88.1	46.0	**68.3**
93	Sample 39 plus lime-sulphur (60)	.....	6.5	34.0	.....	**20.2**	.....	60.7	88.9	.....	**74.8**
57	Commercial calcium arsenate	56.0	8.4	14.4	12.0	**22.7**	85.0	27.1	72.8	44.0	**57.2**
92	Sample 57 plus Bordeaux mixture (61)	52.0	3.3	10.1	12.0	**19.3**	83.0	11.7	72.2	20.0	**46.7**
94	Sample 57 plus lime-sulphur (60)	.....	4.2	37.4	.....	**20.8**	.....	21.0	93.5	.....	**57.2**
25	Laboratory sodium arsenate	99.0	28.8	36.6	33.0	**49.3**	100.0	72.2	91.4	62.0	**81.4**
55	Sample 25 plus Bordeaux mixture (61)	77.0	3.7	33.8	20.0	**33.6**	99.0	43.5	94.2	53.0	**72.4**
23	Commercial zinc arsenite	96.0	12.5	68.9	25.0	**50.6**	100.0	37.5	96.9	44.0	**69.6**
54	Sample 23 plus Bordeaux mixture (61)	83.0	9.1	68.1	18.0	**44.5**	95.0	30.0	98.4	54.0	**69.4**
	Control with food	.0	.0	.6	.0	.....	.0	.0	8.8	12.0	.....

Sample No.	Arsenicals and control.	Percentage of insects dead within—				Toxicity for—				Average toxicity for—	
		10 days.									
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.[1]	All 4 species tested.	Webworms and tent caterpillars.
39	Commercial acid lead arsenate	.....	99.3	100.0	**99.8**	97.0	61.0	66.8	39.5	66.1	63.9
91	Sample 39 plus Bordeaux mixture (61)	100.0	87.0	100.0	**95.7**	92.3	44.8	66.5	29.0	58.2	55.6
93	Sample 39 plus lime-sulphur (60)	.....	88.5	99.6	**94.0**	.....	51.9	74.2	.....	.....	63.0
57	Commercial calcium arsenate	97.0	65.4	100.0	**87.5**	79.3	33.6	62.4	28.0	50.8	48.0
92	Sample 57 plus Bordeaux mixture (61)	97.0	47.5	100.0	**81.5**	77.3	20.8	60.8	16.0	43.7	40.8
94	Sample 57 plus lime-sulphur (60)	.....	76.0	100.0	**88.0**	.....	33.7	76.9	.....	.....	55.3
25	Laboratory sodium arsenate	.....	96.6	100.0	**98.9**	99.7	65.9	76.0	47.5	72.3	71.0
55	Sample 25 plus Bordeaux mixture (61)	100.0	91.3	100.0	**97.1**	92.0	46.2	76.0	36.5	62.7	61.1
23	Commercial zinc arsenite	.....	60.9	100.0	**87.0**	98.7	37.0	88.6	34.5	64.7	62.8
54	Sample 23 plus Bordeaux mixture (61)	100.0	70.9	100.0	**90.3**	92.7	36.7	88.8	36.0	63.5	62.7
	Control with food	.0	2.6	23.1	.....	.....	.....	.....	.....	.....	.....

[1] Based on mortalities for third and sixth days only.

GENERAL AVERAGE TOXICITY.

Four arsenicals without Bordeaux mixture and lime-sulphur {63.5 (all four species). {61.4 (webworms and tent caterpillars).

Four arsenicals with Bordeaux mixture {57.0 (all four species). {55.1 (webworms and tent caterpillars).

Two arsenicals without lime-sulphur, 56.0 (webworms and tent caterpillars).

Two arsenicals with lime-sulphur, 59.1 (webworms and tent caterpillars).

The addition of Bordeaux mixture to the four arsenicals employed reduced the percentages of toxicity against silkworms, webworms, and honeybees, but reduced the toxicity against the tent caterpillars little, if any. The addition of lime-sulphur (sample 93) to the lead arsenate (sample 39) reduced the toxicity against webworms, but seemed to increase it against tent caterpillars. The addition of lime-sulphur (sample 94) to the calcium arsenate (sample 57) neither decreased nor increased the toxicity against webworms, but appeared to increase it against tent caterpillars. In the 1919 results, Bordeaux mixture and lime-sulphur reduced the rates of toxicity in all cases.

The following data are not given in Table 16: Silkworms, 2 sets (each of 50); webworms (*H. cunea*), 1 set (variation 107–332, average 141); tent caterpillars, 3 sets (118–557: 301); and honeybees, 2 sets (each of 50).

To determine the percentage of arsenic borne by leaves sprayed with the foregoing spray mixtures, many apple and mulberry leaves were sprayed at four different periods. The parts of arsenic per million parts of the leaves were as follows: Sample 39, 1,200; sample 91, 800; sample 93, 800; sample 57, 1,000; sample 92, 800; sample 94, 900; sample 23, 1,650; sample 54, 1,300; sample 25, 1,100; and sample 55, 1,100. The general average of those containing neither Bordeaux mixture nor lime-sulphur (samples 39, 57, 23, and 25) is 1,238 parts of arsenic, while those containing these two fungicides (samples 91, 93, 92, 94, 54, and 55) have a general average of 950 parts of arsenic. According to these figures, the fungicides reduced the arsenic content 23.3 per cent, whereas they reduced the general average toxicity only 11.5 per cent.

RELATIVE TOXICITY OF ARSENATES AND ARSENITES.

Toxicologists report that arsenites are more toxic than arsenates. Furthermore, on the basis of equal percentage of arsenious oxid and arsenic oxid, 16.2 per cent more metallic arsenic is present in the arsenites than in the arsenates. To secure additional data on this subject, a high-grade acid lead arsenate, a calcium arsenate, a sodium arsenate, a zinc arsenite, and a Paris green were selected in 1919 for comparison. The following insects were used: Silkworms, 1 set (variation 49–54, average 51); webworms (*H. cunea*), 2 sets (818–1725, average 1173); webworms (*H. textor*), 1 set (189–310, average 251); potato-beetle larvæ, 3 sets (282–404, average 345); and grasshoppers, 2 sets (181–302, average 242). After deducting the mortalities of the controls, the average percentages of toxicity were as follows: Acid lead arsenate (sample 39) 66, calcium arsenate (sample 5) 63.9, and sodium arsenate plus Bordeaux mixture (sample 55) 61.7, an average of 63.9 for the arsenates on five species of insects; zinc arsenite (sample 23) 57.6, and Paris green (sample 64) 65.5, an average of 61.6 for the arsenites. Thus the Paris green tested is equal to the arsenates in toxicity, and, as shown by the average, these two arsenites are not quite as toxic to insects as are the three arsenates employed, although the comparison is not fair in all respects. The smallest number of units eaten were sprayed with Paris green.

TABLE 17.—*Relative toxicity of arsenates and arsenites on 4 species of insects, 1920.*

Sample No.	Arsenicals and control.	Percentage of insects dead within—									
		3 days.					6 days.				
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.	Average.
39	Commercial acid lead arsenate	91.0	11.0	18.1	21.0	35.3	100.0	72.8	82.2	58.0	78.3
25	Laboratory sodium arsenate	99.0	28.8	36.6	33.0	49.3	100.0	72.2	91.4	62.0	81.4
	Average for arsenates	95.0	19.9	27.3	27.0	42.3	100.0	72.5	86.8	60.0	79.9
23	Commercial zinc arsenite	96.0	12.5	68.9	25.0	50.6	100.0	37.5	96.9	44.0	69.6
64	Commercial Paris green	100.0	30.7	65.7	15.0	52.8	.....	85.2	99.0	62.0	86.6
88	.....do	100.0	38.9	59.3	25.0	55.8	.....	86.7	97.5	55.0	84.8
89	.....do	98.0	18.5	53.9	22.0	48.1	100.0	72.3	97.6	57.0	81.7
	Average for arsenites	98.5	22.7	61.9	21.8	51.8	100.0	70.4	97.7	54.5	80.7
90	Commercial London purple	98.0	24.1	34.7	11.0	42.0	100.0	57.1	92.0	33.0	70.5
	Control with food	0.0	0.0	0.6	0.0	.....	0.0	0.0	8.8	12.0	.....

Sample No.	Arsenicals and control.	Percentage of insects dead within—				Toxicity for—				Average toxicity
		10 days.								
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Honeybees.[1]	
39	Commercial acid lead arsenate	.....	99.3	100.0	99.8	97.0	61.0	66.8	39.5	66.1
25	Laboratory sodium arsenate	.....	96.6	100.0	98.9	99.7	65.9	76.0	47.5	72.3
	Average for arsenates	100.0	98.0	100.0	99.3	98.3	63.5	71.4	43.5	69.2
23	Commercial zinc arsenite	.....	60.9	100.0	87.0	98.7	37.0	88.6	34.5	64.7
64	Commercial Paris green	.....	100.0	100.0	100.0	100.0	72.0	88.2	38.5	74.7
88	.....do	.....	100.0	100.0	100.0	100.0	75.2	85.6	40.0	75.2
89	.....do	.....	96.6	100.0	98.9	99.3	62.5	83.8	39.5	71.2
	Average for arsenites	100.0	89.4	100.0	96.5	99.5	60.8	86.5	38.1	71.5
90	Commercial London purple	.....	94.7	100.0	98.2	99.3	58.6	75.6	22.0	63.9
	Control with food	0.0	2.6	23.1	.....	.....	.....	.....	.....	.....

[1] Based on mortalities for third and sixth days only.

In 1920 experiments similar to the preceding ones were performed, using one lead arsenate, one sodium arsenate, one zinc arsenite, three Paris greens, and one London purple (an arsenate and an arsenite combined). The following data, which are not given in Table 17, were obtained: Silkworms, 2 sets (each of 50); webworms (*H. cunea*), 1 set (variation 90–136, average 120); tent caterpillars, 3 sets (207–507, average 288); and honeybees, 2 sets (each of 50). Table 17 shows that the average percentage of toxicity of the arsenates was 69.2, while that of the four arsenites was 71.5. The toxicity of the arsenites should be 16.2 per cent more than that of the arsenates, providing the toxicity is due to the arsenic, irrespective of its form of combination. According to the preceding figures, the toxicity of the four arsenites is only 3.3 per cent more than that of the two arsenates. Comparing the toxicity of the four arsenites with that of the lead arsenate, however, it is 7.8 per cent more,

and comparing the toxicity of the three Paris greens with that of the lead arsenate, it is 11.5 per cent more. London purple (sample 90) has an average percentage of toxicity of 63.9, being practically the same as that of zinc arsenite. While this sample killed all of the webworms tested within 20 days, only about 90 per cent of those fed zinc arsenite died during the same period of time.

RELATIVE TOXICITY OF NEW ARSENATES.

In making a comparison of the relative toxicity of new arsenates, three commercial products and three pure laboratory products were used. The commercial acid lead arsenate (sample 39) was taken as a standard by which to judge the relative toxicity of the other products. The two other commercial products (sample 70, acid lead arsenate made by a new process, and sample 62, magnesium arsenate) and the laboratory sample of barium arsenate (sample 71) are practically new, while the laboratory samples of arsenates of aluminum (sample 73) and of copper and barium (sample 74) are totally new, as far as known.

In 1919 the following insects were tested: Silkworms, 1 set of 50; webworms (*H. cunea*), 1 set (variation 124–195, average 152); webworms (*H. textor*), 1 set (189–514, average 314); potato-beetle larvæ, 2 sets (150–355, average 260); and grasshoppers, 2 sets (181–305, average 265). After deducting the mortalities of the controls, the following figures were obtained. When silkworms, webworms (*H. cunea*), and potato-beetle larvæ were tested, the average percentages of toxicity were: Sample 39 (acid lead), 58.2; sample 70 (acid lead, new process), 57.3; and sample 62 (magnesium), 59. 8. When silkworms, webworms (both species), potato-beetle larvæ, and grasshoppers were tested, the percentages were: Sample 39, 58.8; and sample 62, 54.2. When webworms (both species), potato-beetle larvæ, and grasshoppers were tested, the percentages were: Sample 39, 55; sample 71 (barium), 43.6; and sample 74 (copper and barium), 48.9. When webworms (both species) and potato-beetle larvæ were tested, the percentages were: Sample 39, 57.2; and sample 73 (aluminum), 34.6.

In 1920 these experiments were repeated, with the results shown in Table 18, as well as the following: Silkworms, 2 sets (each of 50); webworms (*H. cunea*), 2 sets (variation 647–897, average 776); webworms (*H. textor*), 1 set (189–514, average 314); honeybees, 2 sets (each of 50); and tent caterpillars, 3 sets (240–556, average 337).

TABLE 18.—*Relative toxicity of new arsenates on 5 species of insects, 1920.*

Sample No.	Arsenates and control.	Percentage of insects dead within—											
		3 days.						6 days.					
		Silkworms.	Webworms (*H. cunea*).	Webworms (*H. textor*).	Honeybees.	Tent caterpillars.	Average.	Silkworms.	Webworms (*H. cunea*).	Webworms (*H. textor*).	Honeybees.	Tent caterpillars.	Average.
39	Commercial acid lead arsenate	91.0	29.9	47.6	21.0	18.1	**41.5**	100.0	95.3	84.2	58.0	82.2	**83.9**
71	Laboratory barium arsenate	22.0	3.2	10.9	11.0	14.0	**12.2**	68.0	68.2	37.3	18.0	75.1	**53.3**
74	Laboratory copper barium arsenate	61.0	10.0	11.7	9.0	18.1	**22.0**	98.0	67.5	57.0	28.0	83.2	**66.7**
62	Commercial magnesium arsenate	91.0	13.8	5.2	4.0	.....	.....	100.0	85.2	46.5	31.0	.....	.....
70	Commercial acid lead arsenate (new process)	91.0	32.9	.....	.....	.....	.....	100.0	88.2	.....	.....	.....	.....
73	Laboratory aluminum arsenate	.....	4.7	7.5	.....	.....	.....	.....	80.8	33.6	.....	.....	.....
	Control with food	0.0	0.0	0.5	0.0	0.6	.....	0.0	0.8	8.5	12.0	8.8	.....

Sample No.	Arsenates and control.	Percentage of insects dead within—					Toxicity for—					Average toxicity.
		10 days.										
		Silkworms.	Webworms (*H. cunea*).	Webworms (*H. textor*).	Tent caterpillars.	Average.	Silkworms.	Webworms (*H. cunea*).	Webworms (*H. textor*).	Honeybees.[1]	Tent caterpillars.	
39	Commercial acid lead arsenate	.....	100.0	100.0	100.0	**100.0**	97.0	75.1	77.3	39.5	66.8	**71.1**
71	Laboratory barium arsenate	92.0	88.2	72.1	99.0	**87.8**	60.7	53.2	40.1	14.5	62.7	**46.2**
74	Laboratory copper barium arsenate	100.0	95.2	82.7	100.0	**94.5**	86.3	57.6	50.5	18.5	67.1	**56.0**
62	Commercial magnesium arsenate	.....	100.0	83.8	.....	.....	97.0	66.3	45.2	17.5	.....	.....
70	Commercial acid lead arsenate (new process)	.....	99.2	.....	.....	.....	97.0	73.4	.....	.....	.....	.....
73	Laboratory aluminum arsenate	.....	98.3	80.9	.....	.....	.....	61.3	40.7	.....	.....	.....
	Control with food	0.0	24.7	16.9	23.1	.....	.....	.....	.....	.....	.....	.....

[1] Based on mortalities for third and sixth days only.

COMPARATIVE AVERAGE TOXICITY.

Sample 39, 72.2; sample 62, 56.5.
Sample 39, 86.0; sample 70, 85.2.
Sample 39, 76.2; sample 73, 51.0.

RELATIVE TOXICITY OF PURE ARSENIC OXIDS AND OF BASES.

In order to judge as accurately as possible the relative toxicity of various bases when combined with the oxids of arsenic, the materials used are grouped in Table 19. In each mixture of the bases, 0.48 gram of the base was used in 100 cubic centimeters of water. At this rate from three to five times as much base was used as is present in the arsenical mixtures.

The following data are not given in Table 19: Silkworms, 1 set (variation 47–54, average 50); webworms (*H. cunea*), 1 set (161–761, average 280); tent caterpillars, 4 sets (565–1030, average 805); and potato-beetle larvæ, 2 sets (105–279, average 152).

TABLE 19.—*Relative toxicity of pure arsenic oxids and of bases on 4 species of insects after deducting mortality of control with food, 1919.*

Sample No.	Material and controls.	Percentage of insects dead within—									
		3 days.					6 days.				
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Average.
9	Arsenious oxid	40.0	21.6	4.6	19.2	**21.4**	58.0	67.3	50.5	23.1	**49.7**
10	Arsenic oxid	100.0	23.1	68.1	65.1	**64.1**	.....	77.6	85.2	65.0	**82.0**
11	Calcium oxid	.0	.0	.0	.1	**.0**	.0	.0	.0	.7	**.2**
5	Calcium arsenate	96.0	12.5	54.3	64.8	**56.9**	100.0	69.2	89.6	63.4	**80.6**
12	Lead oxid	12.8	.0	.0	30.5	**10.8**	31.9	.0	1.5	46.3	**19.9**
39	Acid lead arsenate	96.0	39.1	53.1	50.4	**59.6**	100.0	91.8	86.5	51.2	**82.4**
22	Zinc oxid	.0	.0	.0	4.3	**1.1**	.0	.0	.0	12.0	**3.0**
23	Zinc arsenite	85.7	4.8	73.8	59.8	**56.0**	98.0	32.7	90.0	58.9	**69.9**
63	Magnesium oxid	.0	.0	.....	5.1	.....	.0	.0	.....	5.5	.....
62	Magnesium arsenate	96.0	7.2	.....	73.8	.....	100.0	51.6	.....	70.3	.....
65	Copper oxid	.0	.0	.....	.0	.....	.0	.0	.....	.9	.....
64	Paris green	100.0	18.7	.....	65.7	.....	.....	67.0	.....	64.9	.....
74	Copper barium arsenate	.....	10.0	.....	63.1	.....	.....	66.9	.....	68.9	.....
72	Barium oxid	.....	.0	.....	.0	.....	.....	.0	.....	4.1	.....
71	Barium arsenate	.....	4.3	.....	57.9	.....	.....	43.7	.....	63.4	.....
	Control without food	12.2	.0	.4	.....	.....	61.2	28.7	15.3	.....	.....
	Control with food	.0	.0	1.9	14.6	**4.1**	.0	.6	5.5	20.7	**6.7**
	Control with food, omitting tent caterpillars	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

TABLE 19.—*Relative toxicity of pure arsenic oxids and of bases on 4 species of insects after deducting mortality of control with food, 1919*—Continued.

Sample No.	Material and controls.	Percentage of insects dead within—										Average toxicity.	Units of food eaten per insect (estimated).[2]
		10 days.					20 days.						
		Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Average.	Silkworms.	Webworms (*H. cunea*).	Tent caterpillars.	Potato-beetle larvæ.	Average total percentage dead (control mortalities not deducted).[1]		
9	Arsenious oxid	70.0	95.6	78.9	23.9	**67.1**	86.0	All.	All.	35.1	94.6	**46.1**	9.6
10	Arsenic oxid	.....	94.2	87.6	51.7	**83.4**	.....	All.	All.	All.	100.0	**76.5**	3.5
11	Calcium oxid	.0	.0	1.1	.0	**.3**	.0	.0	0.0	1.7	26.9	**0.2**	143.4
5	Calcium arsenate	.....	92.7	87.7	51.8	**83.0**	.....	All.	All.	All.	100.0	**73.5**	7.4
12	Lead oxid	46.8	.0	4.8	45.7	**24.3**	100.0	4.1	0.0	All.	65.3	**18.3**	148.6
39	Acid lead arsenate	.....	93.7	87.3	45.5	**81.6**	.....	All.	All.	All.	100.0	**74.5**	2.8
22	Zinc oxid	2.0	.0	.0	13.3	**3.8**	6.0	.0	0.0	24.1	35.0	**2.6**	119.8
23	Zinc arsenite	100.0	66.7	86.9	45.6	**74.8**	.....	70.2	All.	All.	97.8	**66.9**	22.0
63	Magnesium oxid	.0	1.3	.....	1.7	.....	.0	2.2	.....	8.6	29.6	.....	105.5
62	Magnesium arsenate	.....	84.7	.....	55.5	.....	.....	74.8	.....	All.	97.9	.....	14.2
65	Copper oxid	2.0	.0	.....	.0	.....	2.0	2.5	.....	0.0	27.0	.....	106.9
64	Paris green	.....	93.7	.....	47.9	.....	.....	All.	.....	All.	100.0	.....	3.9
74	Copper barium arsenate	.....	91.1	.....	54.1	.....	.....	All.	.....	All.	100.0	.....	10.8
72	Barium oxid	.....	6.4	.....	5.1	.....	.....	7.7	.....	8.7	47.2	.....	70.3
71	Barium arsenate	.....	66.9	.....	52.1	.....	.....	66.3	.....	All.	93.7	.....	28.0
	Control without food	71.5	93.6	79.3	.....	.....	100.0	All.	All.	.....	100.0	.....	.....
	Control with food	.0	4.1	12.3	42.5	**14.7**	.0	21.0	50.5	57.1	32.2	**8.5**	100.0
	Control with food, omitting tent caterpillars	.....	.....	.....	.....	.....	.....	.....	.....	.....	26.0	.....	.....

[1] First 8 and next to the last figures to be compared; next 8 and last figures to be compared.
[2] Based on webworms (*H. cunea*) and tent caterpillars.

Comparing the mortality of the insects fed on the various bases with that of the control insects (Table 19), it appears that calcium oxid is beneficial to insects (sample 11, 26.9 per cent, and control, 32.2 per cent), that zinc oxid (sample 22, 35 per cent, and control, 32.2 per cent), magnesium oxid and copper oxid (samples 63 and 65, 29.6 per cent and 27 per cent, and control, 26 per cent) are slightly injurious, that barium oxid (sample 72, 47.2 per cent, and control, 26 per cent) is moderately injurious, and that lead oxid (sample 12, 65.3 per cent, and control, 32.2 per cent) is the most effective of all the bases used.

Since the arsenious oxid (sample 9) used in the 1919 experiments had a low toxicity, a commercial white arsenic (As_2O_3) was used in the experiments conducted in 1920. Sample 9 contained only 17.77 per cent of water-soluble arsenious oxid, while sample 27 contained 38 per cent. To obtain its average toxicity on four species of insects in comparison with the toxicities of pure arsenic oxid (sample 10) and acid lead arsenate (sample 39), the following insects were used: Silkworms, 2 sets (each of 50); webworms (*H. cunea*), 1 set (variation 100–136, average 120); tent caterpillars, 3 sets (221–446, average 292); and honeybees, 2 sets (each of 50). The average percentages of toxicity are as follows: Sample 27 (arsenious oxid), 62.4; sample 10 (arsenic oxid), 74.3; and sample 39 (acid lead arsenate), 71.2.

RELATION OF WATER-SOLUBLE ARSENIC TO TOXICITY OF ARSENICALS.

No perceptible differences in mortality which could be attributed to the usually small differences in water-soluble arsenic oxid were observed in the 14 commercial acid lead arsenates used in the preliminary tests. Three of these arsenates which have high percentages of water-soluble arsenic oxid, however, killed no more insects than the others.

TABLE 20.—*Relation of water-soluble arsenic to toxicity of arsenicals, 1919.*

Sample No.	Arsenicals and control.	Insects tested.		Water-soluble arsenic, based on total arsenic in sample.	Toxicity after deducting mortality of control.	Food eaten per insect (estimated), based on webworms and tent caterpillars.
		Number.	Species.[1]			
				Per cent.	*Per cent.*	*Units.*
18	Laboratory basic lead arsenate	1,184	sftl	1.15	21.5	68.6
28	Commercial basic lead arsenate	1,939	...do	1.73	60.9	10.9
68	Laboratory acid lead arsenate	1,361	...do	.57	59.6	17.6
9	Pure arsenious oxid	1,529	...do	17.77	46.1	9.6
10	Pure arsenic oxid	1,516	...do	100.00	76.5	3.5
23	Commercial zinc arsenite	1,441	...do	1.25	66.9	22.0
70	Commercial acid lead arsenate (new process)	422	sfl	.69	66.9	2.8
39	Commercial acid lead arsenate	2,263	sftlg	.61	68.9	2.9
5	Commercial calcium arsenate	2,645	...do	.41	70.0	9.1
7	....do	2,492	...do	.88	39.9	66.0
56	....do	2,373	...do	1.31	59.2	30.8
57	....do	2,393	...do	.20	60.1	29.9
58	....do	2,114	...do	.52	43.1	68.1
59	....do	2,657	...do	5.20	65.9	18.5
69	Laboratory calcium arsenate	2,298	...do	.88	52.5	55.0
45	Laboratory calcium meta-arsenate	1,232	ft	.04	3.6	99.9
46	Laboratory monocalcium arsenate	1,758	...do	89.26	81.2	2.0
55	Laboratory sodium arsenate plus Bordeaux mixture	2,674	sflgy	.....	61.7	5.0
64	Commercial Paris green	2,059	...do	3.52	65.5	3.2
62	Commercial magnesium arsenate	1,651	flgy	4.64	50.2	18.3
71	Laboratory barium arsenate	1,706	...do	.68	43.6	22.2
74	Laboratory copper barium arsenate	1,814	...do	6.27	48.9	15.6
73	Laboratory aluminum arsenate	1,482	fly	1.91	39.3	16.1
—	Control with food	.....	.....	.....	.....	100.0

[1] s, silkworms; f, webworms (*H. cunea*); t, tent caterpillars; l, potato-beetle larvæ; g, grasshoppers; and y, webworms (*H. tertor*).

Table 20 shows that those arsenicals which are readily water soluble (samples 10 and 46) have extremely high percentages of toxicity, but that some of those which are almost insoluble in water (samples 5, 23, and 39) have percentages of toxicity nearly as high. The toxicity of the insoluble arsenicals does not appear to be based upon the water-soluble arsenic present, but upon the stability of the compound and how readily it can be broken down in the bodies of insects.

During all of these experiments no special study of the burning effects of the many arsenicals sprayed on foliage was made. The percentage of water-soluble arsenic is generally taken as a criterion for judging the burning effect on foliage. The following spray mixtures badly burned wild-cherry foliage: Sodium and potassium arsenates, sodium arsenate plus Bordeaux mixture, all the samples of arsenious and arsenic oxids used. calcium arsenates (samples 5,

34, 46, and 59), lead and calcium arsenates plus lime-sulphur (samples 50 and 51), and Paris green. The following slightly burned wild-cherry foliage: Zinc arsenite (samples 23 and 33), zinc arsenite plus Bordeaux mixture (sample 30), calcium arsenate (sample 32), and barium arsenate (sample 71). Zinc arsenite (sample 23) and Paris green slightly burned mulberry foliage.

RELATION OF ARSENIC RENDERED SOLUBLE BY INSECTS TO TOXICITY OF ARSENICALS.

Kirkland and Smith (*22*), in 1897, found that the alimentary tracts of the gypsy moth larvæ were alkaline to litmus. Analyses of the dialysate from washed and macerated alimentary tracts showed the presence of phosphorus and potash in proportions sufficient to form alkaline potassium phosphate, which is suggested as the cause of the alkaline reaction. Because of the report of these investigators, determinations of the hydrogen-ion concentration (pH value) were made on the water extracts of the bodies of the insects fed various arsenicals and also of the bodies of control insects. The results thus obtained showed a comparatively uniform acidity for all the insects tested. It is possible, however, that lactic or other acids are formed in the dead tissues of the insects. The buffer effect normally available may possibly have masked any slight changes in the reaction caused by the arsenicals fed. It is obvious that the pH data as here obtained, or ash determinations on dialysates of intestinal tracts as made by Kirkland and Smith, are inadequate to show the reactions (pH) of the living tissue of the intestinal tracts of insects.

The following methods were employed to determine the total arsenic and water-soluble arsenic in insects and also the hydrogen-ion concentration of the water extracts from the insects. The weights and number of the washed larvæ were recorded, after which the insects, parts of insects, or feces (dried in an oven at 105° C.) were macerated in a mortar containing about 20 cubic centimeters of distilled water. The macerated larvæ were then transferred to flasks and diluted to 500 cubic centimeters with distilled water. The solutions were shaken every 5 minutes for an hour, at the end of which they were filtered and aliquots were taken for the determination of the hydrogen-ion concentration and for the water-soluble arsenic. The rest of the solution, with the residue, was used for the total arsenic determination. The hydrogen-ion concentration was determined by the indicator method outlined by Clark and Lubs (*8*). The solutions used for determining the soluble arsenic and those with the residues for determining the total arsenic were placed in large porcelain casseroles, and nitric and sulphuric acids were added. They were then warmed on the steam bath and finally heated on the hot plate until the organic material was completely destroyed. Since the acids used, particularly the nitric acid, were not totally free from arsenic, a record of the quantities of acids used was kept. The solutions were then freed from nitric acid by adding water and by applying heat. Next enough water was added to make a volume of 100 cubic centimeters, and finally the arsenic was determined by the Gutzeit method, revised by Smith (*47*).

As preliminary tests, the following experiments were performed in 1919. Both sides of several mulberry leaves were heavily sprayed

with acid lead arsenate (sample 39). After having been dried by an electric fan, the leaves were fed to 50 large hungry silkworms. When the silkworms had ceased eating, they were removed to clean cages where the feces, contaminated as little as possible, were collected and subsequently analyzed. The next morning a sample of 34 dead and dying silkworms was thoroughly washed for five minutes in running tap water, then, one worm at a time, in six different washes, the first four consisting of hydrochloric acid (2 per cent) and distilled water and the last two of distilled water alone. A pencil brush was used for scrubbing them. Analysis of the sixth wash showed the presence of no arsenic. These experiments were repeated five times. To determine how much of the arsenic had passed through the intestinal walls, the alimentary canals of three sets were removed by careful dissections.

The results of the analyses of these samples were as follows: 84 entire silkworms yielded 2.66 milligrams of arsenic oxid, being 54 per cent water-soluble; 72 silkworms with alimentary canals removed yielded 0.89 milligram of arsenic oxid, being 36.7 per cent water-soluble; the alimentary canals of these 72 silkworms yielded 1.03 milligrams of arsenic oxid, being 55.9 per cent water-soluble; and the 2.18 grams of dried feces from these 72 silkworms yielded 0.45 milligram of arsenic oxid. According to the figures obtained from these 72 silkworms, 37.6 per cent of the total arsenic eaten had passed through the walls of the alimentary canals, 43.4 per cent of it was retained inside these canals, and 19 per cent of it was voided with the feces. Reaction (pH) of water extract from the larvæ was neutral (7); from the alimentary canals, slightly alkaline (7.1); from the larvæ with the alimentary canals removed, slightly acid (6.2); and from the feces, acid.

The foregoing experiments were repeated on a larger scale by feeding 13 arsenicals sprayed on leaves to caterpillars of the catalpa-sphinx moth (*Ceratomia catalpæ* Bdv.). The results obtained indicate the following: (*a*) As a general rule, the higher the percentages of water-soluble arsenic in the larvæ and feces, the higher the rates of toxicity of those arsenicals; (*b*) the percentage of water-soluble arsenic in the arsenical ingested usually has little to do with the rate of toxicity; (*c*) the amount of arsenic found per caterpillar is fairly constant for all the arsenicals used; (*d*) the higher the ratio of total arsenic (per 100 grams of larval material or feces) found in the larvæ to that found in the feces, the higher the rate of toxicity; (*e*) the reaction (pH) of water extracts from the larvæ fed various arsenicals seems to bear no relation to the rate of toxicity.

In 1920 the preceding experiments were repeated on a much larger scale, using the following insects: Honeybees, 2 sets (each of 100); silkworms, 3 sets (each of about 25); *Ceratomia*, 2 sets (each of about 25). The procedure followed was the same as that in the preliminary tests, but, in order to determine the percentage of arsenic actually made soluble by the juices of the insects, the percentage under "control results" in Table 21 was subtracted from the percentage of arsenic found soluble in the bodies of insects. Since the solubility of a minute quantity of arsenic in 500 cubic centimeters of water proved to be greater than that of a larger quantity, an amount of arsenic approximating the average amount found in a sample of the insects analyzed was employed as a control.

TABLE 21.—*Relation of arsenic rendered soluble by insects to toxicity of arsenicals, 1919 and 1920.*

Sample No.	Arsenicals.	Total number of insects analyzed.		Percentage of arsenic.							
				Soluble in water on using minute amounts of arsenicals (control results).	Soluble in bodies of—			Made soluble by juices of—			
		Sets.	Individuals.		Honeybees.	Silkworms.	*Ceratomia.*	Average.	Honeybees.	Silkworms.	*Ceratomia.*	Average.
39	Commercial acid lead arsenate	8	310	17.3	44.5	46.0	83.5	**58.0**	27.2	28.7	66.2	**40.7**
28	Commercial basic lead arsenate	8	353	7.2	28.8	37.7	63.5	**43.3**	21.6	30.5	56.3	**36.1**
57	Commercial calcium arsenate	8	405	35.7	78.6	60.6	84.7	**74.6**	42.9	24.9	49.0	**38.9**
27	Commercial white arsenic	7	320	5.2	64.8	33.9	20.0	**39.6**	59.6	28.7	14.8	**34.4**
71	Laboratory barium arsenate	8	360	30.5	69.4	30.3	64.0	**54.6**	38.9	.0	33.5	**24.1**
45	Laboratory calcium meta-arsenate	6	336	2.4	41.8	39.1	22.6	**34.5**	39.4	36.7	20.2	**32.1**
64	Commercial Paris green	9	423	15.9	98.3	44.3	71.0	**71.2**	82.4	28.4	55.1	**55.3**
64C	Sample 64 plus lime (2 grams)	7	321	11.0	91.8	37.4	61.2	**63.5**	80.8	26.4	50.2	**52.5**
62	Commercial magnesium arsenate	9	546	37.9	80.3	59.9	98.7	**79.6**	42.4	22.0	60.8	**41.7**
90	Commercial London purple	6	293	33.2	84.3	48.4	95.1	**75.9**	51.1	15.2	61.9	**42.7**
23	Commercial zinc arsenite	6	292	6.0	58.4	63.8	73.9	**65.4**	52.4	57.8	67.9	**59.4**
74	Laboratory copper barium arsenate	10	570	6.2	74.6	59.2	58.8	**64.2**	68.4	53.0	52.6	**58.0**
10	Pure arsenic oxid	7	331	100.0	88.4	70.9	89.6	**83.0**	.....	.....	.....	.....
25	Laboratory sodium arsenate	9	515	100.0	73.4	54.4	89.7	**72.5**	.....	.....	.....	.....

Sample No.	Arsenicals.	Toxicity based on honeybees and silkworms.	Water-soluble arsenic, based on total arsenic in sample.	Average amount of arsenic per insect analyzed.				Average reaction (pH) of water extract from insect material.
				Honeybees.	Silkworms.	*Ceratomia*	Average.	
			Per ct.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	
39	Commercial acid lead arsenate	78.5	0.61	0.0223	0.1212	0.0126	**0.0520**	6.0
28	Commercial basic lead arsenate	61.7	1.73	.0142	.0803	.0158	**.0368**	6.0
57	Commercial calcium arsenate	65.5	.20	.0099	.1245	.0189	**.0511**	6.0
27	Commercial white arsenic	69.5	38.00	.0091	.0914	.0285	**.0430**	6.0
71	Laboratory barium arsenate	51.0	.68	.0105	.0694	.0138	**.0312**	5.8
45	Laboratory calcium meta-arsenate	17.6	.04	.0120	.0676	.0110	**.0302**	5.9
64	Commercial Paris green	79.5	3.52	.0087	.1203	.0143	**.0478**	5.9
64C	Sample 64 plus lime (2 grams)	66.7	3.52	.0075	.1157	.0276	**.0503**	5.8
62	Commercial magnesium arsenate	71.0	4.64	.0120	.1460	.0173	**.0584**	6.0
90	Commercial London purple	73.7	5.30	.0068	.1315	.0305	**.0563**	5.8
23	Commercial zinc arsenite	77.5	1.25	.0132	.1430	.0220	**.0594**	6.0
74	Laboratory copper barium arsenate	66.0	6.27	.0058	.0675	.0177	**.0303**	6.0
10	Pure arsenic oxid	78.5	100.00	.0165	.1130	.0600	**.0632**	5.9
25	Laboratory sodium arsenate	82.4	100.00	.0180	.0968	.0169	**.0439**	5.9

The following deductions are made from the results shown in Table 21:

(*a*) Samples 45, 27, 23, 74, and 28 are very stable in water (slightly soluble as compared with control results); samples 64C, 64, and 39 are moderately stable in water; samples 71, 90, 57, and 62 are unstable in water; and samples 10 and 25 are totally water soluble.

(*b*) Sample 45 is least soluble and sample 10 is most soluble in the bodies of insects. Samples 10 and 25 were totally water soluble before they were eaten, but after being eaten only about three-fourths of the arsenic was obtained as soluble arsenic.

(*c*) While no general deductions can be made as to the average percentages of arsenic found soluble in the bodies of insects, when the figures under "control results" are subtracted from these averages, as a general rule, the higher the percentages of arsenic made soluble by the juices of the insects, the higher are the rates of toxicity. Using lead arsenate (sample 39) as a standard, the last statement is strongly supported by the results obtained with the first seven arsenicals (samples 39, 28, 57, 27, 71, 45, and 64), but it is not so strongly supported by the following five samples (64C, 62, 90, 23, and 74).

(*d*) The percentages of water-soluble arsenic in the original samples of arsenicals bear no relation to the toxicity of those arsenicals, except in the case of those which are totally water soluble.

(*e*) As a general rule, the larger the average amount of arsenic in the insects analyzed, the higher is the rate of toxicity of that arsenical. Using average weights of the undried insects fed on all 14 of the arsenicals and average amounts of arsenic per insect, a bee weighing 98 milligrams contained 0.0119 milligram of arsenic, a silkworm weighing 1,370 milligrams contained 0.1063 milligram, and a *Ceratomia* weighing 1,620 milligrams contained 0.0219 milligram of arsenic. Thus, although a silkworm is 14 times as large and a *Ceratomia* is 16 times as large as a bee, the silkworm contained 9 times as much arsenic as did the bee and 5 times as much as did the *Ceratomia*. This difference in amount of arsenic probably may be explained by the fact that for bees and silkworms the spray mixtures were used five times the usual strength, while for the *Ceratomia* the usual strength (1 pound to 50 gallons of water) was sufficient to kill the insects within 24 hours.

(*f*) None of the water extracts of the bodies of the insects fed on the various arsenicals showed an alkaline reaction, and the highest acid reaction was 5.8 (pH value). As an average pH value for the 14 arsenicals, the bees gave a value of 6; the silkworms, 5.7; and the *Ceratomia*, 6.1; and as an average pH value for any arsenical against all three insects, the only figures obtained are 5.8, 5.9, and 6. Again it is shown that the pH value has nothing to do with the percentage of arsenic rendered soluble by the insect juices.

Experiments like those performed on the three foregoing species of insects were also performed on another large but easily killed caterpillar (*Datana integerrima* G. & R.). As the number of these caterpillars was limited, only samples 39, 57, and 64 were used against this species, so that the results obtained could not be easily incorporated in Table 21. They are, however, similar in all respects to those already discussed.

MINIMUM DOSAGE OF LEAD ARSENATE REQUIRED TO KILL SILKWORMS.

By means of a needle-pointed pipette, an acid lead arsenate (sample 39) was dropped upon fresh mulberry leaves. Upon evaporation of the water from these drops, the portions of leaves bearing the white spots were fed to large hungry silkworms in the last instar.

One drop would occasionally kill a large worm but more often two drops were fatal. In almost every case three drops proved fatal within 24 hours. Therefore, for these larvæ three drops may be regarded as a minimum fatal dosage of acid lead arsenate. An analysis of 100 drops (4 sets) from the same pipette gave 0.0091 milligram of metallic arsenic as an average per drop, making 0.0273 milligram of arsenic a minimum fatal dosage for fully grown silkworms.

An analysis of 59 of the dead silkworms, each of which had eaten three drops of the arsenical, gave 0.0027 milligram of arsenic per larva, indicating that 90 per cent of the arsenic eaten had been voided in the feces before the larvæ died. Silkworms which had received a maximum dosage of the same arsenical voided in the feces only 19 per cent of the arsenic eaten, and *Ceratomia*, which had received an average dosage of the same poison, voided 64 per cent of the arsenic with the feces.

QUANTITY OF ARSENIC EATEN BY INSECTS IN FEEDING TESTS.

During the feeding tests many samples of dead larvæ were prepared for analyses, but only those of webworms (*H. textor*) and those of potato-beetle larvæ were finally analyzed. The webworm is one of the most difficult to kill by arsenic, while the potato-beetle larva is one of the most easily killed. Some of the webworms were washed as described on page 44, but most of them were not washed. Also several samples of feces (more or less contaminated) were analyzed. The percentage of toxicity, as shown in Table 22, is the average of the mortalities recorded on the third, sixth, and tenth days for the one species concerned.

TABLE 22.—*Arsenic consumed by insects in feeding tests, 1919.*

Species of insects and sample No.	Arsenicals and controls.	Condition of larvæ before being analyzed.	Number of larvæ analyzed.	Arsenic per larva.	Arsenic (parts per million) in—		Toxicity after deducting mortality of control.
					Larvæ.	Feces.	
Webworms (*H. textor*):				*Milligrams.*			
39	Commercial acid lead arsenate.	Washed and dried.	163	0.0017	359	527	.....
39	....do	Dried	400	.0025	385	1,114	68.6
5	Commercial calcium arsenate.	Washed and dried.	200	.0014	303	746	.....
5	....do	Dried	400	.0024	481	1,125	59.1
28	Commercial basic lead arsenate.	....do	200	.0040	691	330	48.9
69	Laboratory calcium arsenate.	....do	180	.0033	436	851	15.1
69B	Sample 69 plus 1 gram lime per 418 cc.	....do	130	.0040	674	355	6.3
71	Laboratory barium arsenate.	....do	160	.0027	399	365	31.5
62	Commercial magnesium arsenate.	....do	200	.0050	747	539	36.5
55	Laboratory sodium arsenate plus Bordeaux mixture.	....do	200	.0016	303	818	59.3
23	Commercial zinc arsenite.	....do	200	.0055	917	903	63.6
64	Commercial Paris green.	....do	200	.0050	911	946	62.6
73	Laboratory aluminum arsenate.	....do	200	.0028	383	840	32.0
74	Laboratory copper barium arsenate.	....do	200	.0053	613	306	41.8
	Control feces					15	

TABLE 22.—*Arsenic consumed by insects in feeding tests, 1919*—Continued.

Species of insects and sample No.	Arsenicals and controls.	Condition of larvæ before being analyzed.	Number of larvæ analyzed.	Arsenic per larva.	Arsenic (parts per million) in—		Toxicity after deducting mortality of control
					Larvæ.	Feces.	
Potato-beetle larvæ:				*Milligrams.*			
39	Commercial acid lead arsenate.	do	150	0.0017	141	.....	62.1
28	Commercial basic lead arsenate.	do	125	.0020	168	.....	53.4
68	Laboratory acid lead arsenate.	do	100	.0038	327	.....	57.9
5	Commercial calcium arsenate.	do	150	.0026	205	.....	62.7
69	Laboratory calcium arsenate.	do	110	.0043	311	.....	61.8
69B	Sample 69 plus 1 gram lime per 418 cc.	do	80	.0042	330	.....	61.9
71	Laboratory barium arsenate.	do	110	.0049	350	.....	50.9
62	Commercial magnesium arsenate.	do	130	.0029	223	.....	57.1
55	Laboratory sodium arsenate plus Bordeaux mixture.	do	100	.0028	257	.....	51.8
23	Commercial zinc arsenite.	do	100	.0018	172	.....	54.7
64	Commercial Paris green	do	120	.0024	206	.....	59.5
74	Laboratory copper barium arsenate.	do	130	.0051	460	.....	54.7

The following facts are evident from Table 22: About 40 per cent of the arsenic (samples 39 and 5) found in the samples of webworms was probably carried on the integuments of the larvæ. As a general rule, the higher the average toxicity, the smaller is the quantity of arsenic found in the larvæ. The ratio of arsenic found in the webworms to that found in their feces is about 3 to 5 for those arsenicals giving high toxicities, while for those arsenicals giving low toxicities the ratio is about 1 to 1.

PHYSIOLOGICAL EFFECTS OF ARSENIC ON INSECTS.

Symptoms of arsenic poisoning in the various insects used in the preceding experiments can not be fully described, because these insects were usually too sluggish to permit observation of the later symptoms, other than an occasional contortion of the body, the voiding of soft, watery feces, spewing at the mouth, and finally the complete loss of control of the legs.

Since honeybees are extremely active and are easily studied in observation cases, they were fed arsenic acid (sample 10) in honey at the rate of 0.00076 milligram of arsenic oxid or 0.0005 milligram of metallic arsenic per bee, providing all consumed equal quantities of the poisoned food. The poisoned bees lived for 5.4 days on an average, while the controls lived for 8.4 days on an average. On the second day after being poisoned many of these bees became more or less inactive, a few died, and subsequently but few of them were seen eating. By the third day they were dying rapidly, their abdomens

were swollen, and they could not fly, although they could walk in a staggering manner, dragging their abdomens on the table. The only difference between the behavior of the bees subjected to nicotine poisoning (*29*, p. 91) and that of bees subjected to arsenic poisoning is that (*a*) nicotine acts more quickly, (*b*) its symptoms are more pronounced, and (*c*) in arsenic poisoning the abdomen is always more or less swollen, while in nicotine poisoning the abdomen is only rarely swollen. From the symptoms observed, it may be concluded that the bees fed arsenic might have died of motor paralysis, although the paralysis may be only a secondary cause.

Blythe (*4*, p. 567) says that flies, within a few minutes after eating arsenic borne on common arsenical fly paper, fall, apparently from paralysis of the wings, and soon die. Spiders and all insects into which the poison has been introduced exhibit a similar sudden death.

According to the textbooks on pharmacology by Cushny (*14*) and Sollmann (*49*), arsenic is termed, among other things, "a capillary poison." These authors state that arsenic is toxic to all animals having a central nervous system and also to most higher plants, but not to all the lower organisms. In mammals arsenic is cumulative, being stored in various organs, and it is excreted very slowly by the usual channels—urine, feces, sweat, milk, epidermis, and hair. With oral administration, the main part leaves by the feces, probably having never been dissolved.

TRACING ARSENIC IN TISSUES OF INSECTS.

All attempts to trace arsenic fed alone to fall webworms (*H. cunea*) by histological methods failed. The light-colored precipitate formed by the union of arsenic and silver nitrate was either washed out of the tissues or was obscured because the tissues were stained dark by the silver nitrate.

In an endeavor to trace arsenic in both the soluble and insoluble forms by stains and lampblack the following experiments were performed, using the method for tracing nicotine outlined by McIndoo (*29*, p. 106–109).

Four sets of fall webworms were fed leaves sprayed with an acid lead arsenate (sample 39), mixed with stains or lampblack as follows: First set ate arsenate mixed with indigo-carmine; second set ate arsenate mixed with carminic-acid; third set ate arsenate mixed with No. 100 carmine powder; and fourth set ate arsenate mixed with No. 100 lampblack powder. A day later those fed carmine were voiding reddish feces, and two days after being fed all of those nearly dead were fixed in absolute alcohol. The indigo-carmine and carminic-acid were soluble in water, but they were partially precipitated by absolute alcohol; the carmine was only slightly soluble in water, but totally insoluble in absolute alcohol; and the lampblack was soluble in neither water nor absolute alcohol.

Webworms fed indigo-carmine showed no stain. Those fed carmine-acid and carmine revealed pinkish intestines, those colored with the carmine being almost red. The intestinal contents of these larvæ were pink, but no carmine-acid could be observed outside the intestinal wall. In the larvæ fed carmine the stain was widely distributed. The nuclei in the cells of the intestine were strongly

stained, while all the tissues outside the intestinal wall contained more or less of the stain. In the larvæ fed lampblack much of the powder could be observed inside the intestine, but very little (perhaps none in reality) outside the intestinal wall.

GENERAL PROPERTIES OF ARSENICALS.

Used alone, arsenious oxid burns the most resistant foliage, because of its high percentage of water-soluble arsenious oxid. To overcome this difficulty, Sanders and Kelsall (*43*) mixed a very finely divided arsenious oxid with Bordeaux mixture, to serve as a substitute for sodium arsenate and Bordeaux mixture, to control the potato beetle and late blight in Nova Scotia. Cooley (*13*) suggested the use of white arsenic with Bordeaux mixture for dusting potato vines and has successfully used white arsenic as a substitute for the expensive Paris green in bran mash to control grasshoppers in Montana. He considers crude arsenious oxid to be superior to the refined product, as the particles are finer. Most authors think that arsenious oxid possesses high insecticidal properties. The results of the investigation here reported, however, indicate that the toxicity of arsenious oxid varies greatly, depending on the degree of fineness of the crystals which influences the percentage of water-soluble arsenious oxid present. In no case did the toxicity equal that of an equivalent amount of arsenic oxid present in acid lead arsenate.

Acid lead arsenate, a satisfactory insecticide material, is to be recommended in general when an uncombined arsenical is to be used, as it possesses excellent adhesive and insecticidal properties, and burns foliage little if at all. Acid lead arsenate is compatible with Bordeaux mixture and with nicotine sulphate solutions. Lime-sulphur and acid lead arsenate are incompatible from a chemical standpoint, some soluble arsenic being formed. However, it is well recognized that acid or basic lead arsenates are used with lime-sulphur without serious foliage injury in most cases. A powdered acid lead arsenate contains about 32 per cent of arsenic oxid and about 64 per cent of lead oxid, while powdered basic lead arsenate contains about 23 per cent of arsenic oxid and about 73 per cent of lead oxid. Also, basic lead arsenate is more stable and less toxic than acid lead arsenate.

Paris green, a valuable insecticide on account of its high arsenic content, is said to dust well in spite of its high apparent density, but not to adhere well to foliage. It has no advantages over acid lead arsenate, but has several disadvantages, the burning of foliage being the principal one. The expensive copper sulphate and acetic acid used in its manufacture do not increase its power as a poison.

The amount of soluble arsenic in an arsenical is reduced by mixing it with Bordeaux mixture, and an unsafe arsenical may in certain cases be made safe by mixing it with Bordeaux.

Soaps contain alkalies which decompose arsenicals. The more soap used, the greater the decomposition. When calcium arsenate was mixed with sodium fish-oil soap, a smaller amount of soluble arsenic was formed than when acid lead arsenate was used in the mixture. Both of these mixtures are incompatible.

When acid lead arsenate or calcium arsenate is used in a kerosene-soap emulsion, soluble arsenic is rapidly formed. In the acid lead

arsenate combination, six times as much arsenic is formed as in the calcium arsenate combination. Acid lead arsenate, therefore, should not be used in preparing kerosene-emulsion sprays, as the mixture is chemically incompatible. Gray (*16*) reports that basic lead arsenate is not affected by the alkali of soap.

When acid lead arsenate was mixed with solutions of nicotine sulphate, no chemical incompatibility was found. When calcium arsenate was used with nicotine sulphate, however, the latter was decomposed and free nicotine was formed. The SO_4 of the nicotine sulphate combined with free lime (CaO), if present, or with lime of the calcium arsenate, and large amounts of soluble arsenic were formed in certain mixtures. Free nicotine is present in all of these mixtures. The free nicotine is not dangerous but the soluble arsenic is. These mixtures are chemically incompatible. The findings in connection with the chemical compatibilities and incompatibilities of the various arsenicals, fungicides, and other materials tested are summarized in Table 23. Gray (*16*) in 1914 published a summary of data on the compatibilities of various spray materials which he had collected.

TABLE 23.—*Chemical compatibility of arsenicals combined with other spray materials.*

Arsenicals used.	Other spray materials used.				
	Lime sulphur.	Bordeaux mixture.	Kerosene emulsion.	Sodium fish-oil soap.	Nicotine-sulphate solution.
Acid lead arsenate	Incompatible	Compatible	Incompatible	Incompatible	Compatible.
Calcium arsenate	Compatible	do	do	do	Incompatible.
Paris green		do			
Sodium arsenate		do			

Sanders and Brittain (*41*) tested the comparative insecticidal properties of the arsenates of calcium, barium, and lead, alone and in combination with Bordeaux mixture, lime-sulphur, barium tetrasulphid, and sodium sulphid ("soluble sulphur"), on one species of insects. The results obtained showed that the presence of a fungicide had a marked influence on the efficiency of the arsenical investigated. The four arsenicals were 13 per cent more efficient when used with sodium sulphid than when used alone. The toxicity of the arsenicals was reduced when they were mixed with any of the other fungicides. The explanation given by these authors for the increased toxicity resulting from the use of sodium sulphid with an arsenical is that the sodium increases the palatability of the sprayed leaves, which causes the insects to eat ravenously for a few days. The insects thus take a large amount of arsenic into their systems in a short time and death rapidly ensues.

Mixing sodium sulphid with acid lead arsenate produces some lead sulphid and sodium arsenate. The sodium arsenate is soluble and therefore may be more active than the original acid lead arsenate. The results in Table 21 indicate that the soluble arsenicals are more toxic per unit of arsenic than are the insoluble ones, the greater toxicity being due to the water-soluble arsenic present in the compound or to the arsenic which is quickly rendered soluble inside the insects. Data obtained during this investigation suggest that the amount of arsenic present per unit of sprayed leaf is larger when a

soluble arsenical is used in combination with a fungicide than when an insoluble arsenical is used. Accordingly it may be possible to explain chemically the increased activity or efficiency when sodium sulphid is used with arsenicals.

Evidence seems to show that it is not always true that an insecticide containing a high percentage of arsenic is more toxic than one containing less arsenic, for the reason that toxicity depends not alone upon the amount of arsenic present, but also upon its form of combination. The insecticidal rôle played by the base itself is small and sometimes nonexistent.

When lime or Bordeaux mixture was combined with the arsenicals the toxicity of the arsenicals was reduced. The fact that the addition of lime or Bordeaux mixture to the arsenicals reduced the toxicity of these insecticides to insects may be explained in two ways: (*a*) Leaves sprayed with the arsenicals combined with lime or Bordeaux usually contained less arsenic than those similarly sprayed with the arsenicals alone; (*b*) the toxicity was greater in the tests with honeybees fed honey containing the arsenicals alone than in tests in which bees ate honey containing the arsenicals with lime or Bordeaux mixture. These results support the theory that the calcium present prevents or counteracts the formation of soluble or more toxic arsenic compounds.

Based on the reported results, it would appear that if all seven species of insects used had been tested under similar conditions, their susceptibility to an acid lead arsenate would probably be in the following order, beginning with the insect most susceptible: Honeybees, silkworms, grasshoppers, potato-beetle larvæ, tent caterpillars, webworms (*H. textor*), and webworms (*H. cunea*).

The arsenious oxid ("white arsenic") samples were crystalline; the other commercial arsenicals generally lacked crystal outline and were probably for the most part amorphous. The calcium arsenates used contained some small "octahedral" crystals, but were largely composed of apparently amorphous material. The arsenious oxid samples gave variable results in the toxicity studies and wide variations were found in the results when calcium arsenates were used. On the other hand, the amorphous acid lead arsenates and the amorphous Paris green samples gave uniform toxicity data. The data show a relation between the uniformity of the products and uniformity of toxicity. Where the products were not uniform variations in toxicity were found.

Commercial arsenicals used for spraying or dusting purposes are usually judged chemically on the basis of the total arsenious or arsenic oxid contents and on the percentages of the total amount of these oxids which go into solution under certain conditions. The percentage of base present is also determined. Soluble arsenic oxids or arsenic rendered soluble after the application of arsenicals will burn foliage, the extent of the injury depending mainly on the amount of soluble oxid present or formed in the spray or solution applied. The results here reported indicate that it is the soluble arsenic or the arsenic rendered soluble by the insects that causes death. The rapidity with which arsenicals are made soluble in the bodies of insects seems to be the most important factor in connection with their toxicity. What happens to the soluble arsenic inside the insects is not known, except that part of it passes through the in-

testinal walls into the blood and is distributed to all parts of the body. A small portion of it reaches the nervous system, where it apparently kills by paralysis. The way arsenic affects the various tissues is not known, although Sollmann (*49*) reports that it is now generally believed that the arsenicals hinder protoplasmic oxidation in an unknown way. A successful insecticide must be sufficiently stable to be applied to foliage without injury and sufficiently unstable to be broken down in appreciable amounts in the bodies of the insects ingesting it.

SUMMARY.

Arsenious oxid, commercially known as white arsenic, or simply as arsenic, is the basis for the manufacture of all arsenicals. Samples of commercial arsenious oxid vary in purity, fineness, apparent density, and in the rate of solution in water (soluble arsenic), which accounts for the diverse chemical and insecticidal results reported in the literature. Arsenites are prepared by combining arsenious oxid with a base. Arsenates are produced by first oxidizing arsenious oxid to arsenic oxid (arsenic acid) and then combining the material with a base. Except for their water content of approximately 50 per cent, the paste arsenicals have the same general composition as the powdered arsenicals.

The usual lead arsenate on the market, acid lead arsenate ($PbHAsO_4$), is well standardized and stable. Basic lead arsenate ($Pb_4PbOH(AsO_4)_3$), also well standardized and stable, is being manufactured at present only to a limited extent. Chiefly because of its low arsenic and high lead contents, basic lead arsenate is more stable and therefore less likely to burn foliage than acid lead arsenate. It possesses weaker insecticidal properties and is somewhat more stable in mixtures than acid lead arsenate.

Commercial calcium arsenate (arsenate of lime), the manufacture of which is rapidly becoming standardized, contains more lime than is required to produce the tribasic form.

Paris green, an old and well standardized arsenical, is less stable and contains more "soluble arsenic" than commercial arsenates of lead or lime.

Laboratory samples of aluminum arsenate, barium arsenate, and a copper barium arsenate mixture, in the powdered form, were tested. The last named gave excellent insecticidal results.

The following combinations of insecticides and fungicides were found to be chemically compatible: Lime-sulphur and calcium arsenate; nicotine sulphate and lead arsenate; and Bordeaux mixture with calcium arsenate, acid lead arsenate, zinc arsenite, or Paris green. The following combinations were found to be chemically incompatible: Soap solution with either calcium arsenate or acid lead arsenate; kerosene emulsion with either calcium arsenate or acid lead arsenate; and lime-sulphur with acid lead arsenate.[9] Combined with nicotine sulphate, calcium arsenate always produces free nicotine, and unless a decided excess of free lime is present soluble arsenic is produced.

The combination of sodium arsenate with Bordeaux mixture as used in the experiments here reported gave no soluble arsenic.

[9] According to the Bureau of Entomology, this combination in large amounts is used successfully in the field.

Of all the arsenicals tested, acid lead arsenate and zinc arsenite were the most adhesive and Paris green the least adhesive on potato foliage. The use of lime with arsenicals applied to potato foliage did not increase their adhesiveness.

The suspension properties of the powdered arsenicals are of value in differentiating "light" from "heavy" powders, as determined by their apparent densities.

The physical properties of the commercial powdered arsenicals could not be satisfactorily determined by sieving, as they are generally amorphous and pack in the sieve on shaking. Arsenious oxid samples sometimes contain or consist of relatively coarse crystals, so that sieving may provide valuable data.

Microscopic examination gave little information concerning the desirable physical properties of the amorphous or seemingly amorphous powdered arsenicals. Differences in size of crystals present in the arsenious oxid samples were detected under the microscope.

The toxicity findings are based on the use of equivalent quantities of arsenious and arsenic oxids. Higher percentages of toxicity were found for acid lead arsenate than for basic lead arsenate. The different samples of calcium arsenate tested varied widely in toxicity. When lime or Bordeaux mixture was added to arsenicals, the toxicities were reduced. The average toxicity of the three samples of Paris green and that of one zinc arsenite tested was slightly more than that of an acid lead arsenate and a sodium arsenate. Of the four samples of arsenites, the Paris green samples gave the highest values, zinc arsenite being much less toxic. Based on equivalent metallic arsenic percentages, the Paris green samples gave values no higher than that of the acid lead arsenate tested. Several new arsenates tested did not show as high toxicities as did acid lead arsenate. Of the various bases tested, lead oxid showed some insecticidal value, while the oxids of zinc, magnesium, and copper showed little and lime no value. Arsenic acid, acid lead arsenate, and one sample of calcium arsenate gave high and practically equal toxicities. Arsenious oxid (white arsenic) gave lower and variable results. The percentages of water-soluble arsenic in the original arsenicals had little or no influence on the toxicity, except in the case of those arsenicals which were entirely or largely water soluble. These had high percentages of toxicity.

The determination of reaction in terms of the pH value of water extracts from the bodies of various insects fed all of the different arsenicals, and also from the bodies of control insects, showed uniformly a slight acidity. These results indicate that the arsenic compounds fed did not affect the pH values as determined on dead insects.

The minimum dosage of metallic arsenic required to kill a honeybee is approximately 0.0005 milligram, while 0.0273 milligram (or 54 times as much) is required to kill a full-grown silkworm. Honeybees, confined in cases, void none of the arsenic eaten, whereas silkworms void 90 per cent of the amount ingested. Thus, in reality about 6 times, rather than 54 times, as much arsenic is fatal to a silkworm as is required to kill a honeybee under the somewhat unnatural living conditions.

The conclusions that may be drawn from this investigation are that a chemical analysis of an arsenical does not give sufficient data to judge satisfactorily its insecticidal properties, and a toxicity study alone does not show that an arsenical is suitable for general insecticidal purposes, but both a chemical analysis and a thorough toxicity study are required in order to judge whether or not an arsenical is a satisfactory insecticide.

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